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Thermal alterations of potassium exchangeability in micaceous mineral particles of different size

Jia Shung Wang
Iowa State University

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THERMAL ALTERATIONS OF POTASSIUM EXCHANGEABILITY IN
MICACEOUS MINERAL PARTICLES OF DIFFERENT SIZE

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Thermal alterations of potassium exchangeability in
micaceous mineral particles of different size

by

Jia Shung Wang

A Dissertation Submitted to the
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Ames, Iowa

1981

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I. INTRODUCTION

Micaceous minerals contain large amounts of K that is located between their contracted layers. By releasing this K from its interlayer location to more accessible particle surfaces or the surrounding solution, these minerals can provide an important natural source of K for growing plants in many soils. Thus, the processes and factors governing the release of interlayer K have been given a great deal of attention.

Interlayer K in micaceous minerals can be replaced by hydrated cations that induce an expansion of the mineral. The degree of this exchange of K is governed by the chemical environment imposed by the solution surrounding the mineral particles and by various characteristics of the minerals themselves. The effects of the solution phase on the exchange of interlayer K have been established well enough that they can be largely controlled. When this is done, it is evident that the various micaceous minerals still exhibit major differences in K release behavior. To delineate the mineral parameters responsible for these variations in K release behavior, comparisons of several minerals that have a range of properties are often relied upon. Another approach involves the use of mineral treatments that produce simultaneous changes in the exchangeability of interlayer K and various relatable mineral properties. Thermal treatments

have proven useful in this regard.

Substantial changes in K release behavior have been observed with coarsely ground mica samples that have been exposed to various heat treatments. The effects of thermal treatments on muscovite are quite different from those observed with heated trioctahedral micas and are well-suited for a search of relationships between K release behavior and specific mineral properties. By measuring the weight loss that occurs in heated muscovite samples, some of the associated changes in K release have been related to the occurrence of dehydroxylation, whereas, X-ray diffraction studies have emphasized the impact that small changes in the basal spacings of heated muscovite can have on interlayer K release. On the other hand, thermally induced reductions in the rate of interlayer K release in muscovite have not been explained. Indeed, the results obtained so far with heated micas have been limited by the use of just a few ground samples. To obtain more information about the mineral properties governing K release, the experiments with thermally altered micas need to be expanded to include a variety of muscovite and related mineral samples that might respond quite differently to the thermal treatments.

Particle size has a complex effect on the exchangeability of interlayer K in micas. A reduction in particle size usually enhances the rate with which some of the K can be replaced

but can also inhibit the exchange of part of the K. The incomplete exchange of interlayer K in fine-grained micaceous minerals is referred to as the "small particle effect" and has been attributed to the influence an expansion of some layers (by K release) can exert on adjacent layers that are still contracted. A similar situation of mixed layering (expanded and contracted layers) can exist in coarse and fine particles of some naturally occurring micaceous minerals. Thus, by grinding micas to different particle sizes and selecting naturally occurring micaceous minerals that differ in particle size and degrees of mixed layering, a variety of related mineral samples that differ in K release behavior can be assembled rather easily for a more extensive thermal study of the K release process.

In this investigation, muscovite and related micaceous mineral samples that differed in particle size and mixed layering were exposed to various thermal treatments and examined for mineral alterations and changes in K release behavior. Relationships between these thermally induced changes in the mineral samples were used to ascertain the role of mineral properties in interlayer K release.

II. LITERATURE REVIEW

A. Characteristics of Micaceous Minerals

Concepts regarding the structure of micaceous minerals are largely based on information obtained with macro-crystalline micas. It is very difficult to characterize microcrystalline micaceous minerals because of their small grain size and variable degree of crystal imperfections. The first complete structural analysis of mica was made by Jackson and West (1933) using X-ray diffraction methods. In recent years, many refinements in the structure of these minerals have been obtained with modern instruments and technology (Radoslovich, 1960; Steinfink, 1962; Giese, 1979).

1. Mica

Micas are 2:1 type layer silicate minerals. Each layer is composed of two tetrahedral sheets with one octahedral sheet sandwiched between. The tetrahedra consist of Si atoms surrounded by four oxygen atoms, three of which are shared with other tetrahedra. These shared oxygens link together to form an idealized hexagonal network and are often referred to as the basal oxygens. The fourth oxygen (apical oxygen), which is not shared with other tetrahedra, lies on one side of the plane of shared oxygens and constitutes part of the octahedral sheet. The octahedra consist of four oxygens (apical oxygens of the tetrahedra sheet) and two

hydroxyls that are grouped around various cations and are linked together to form sheets by sharing anion pairs along the edges of the polyhedra. The layers are stacked together with the planes of basal oxygens facing each other and separated by an interlayer space.

Isomorphous substitution of Al for as much as one-fourth of the Si in the tetrahedral sheet gives rise to a charge deficit (layer charge) which is primarily balanced by K in the interlayer space. These interlayer K ions lie between the hexagonal rings of basal oxygens and electrostatically bind the silicate layers together.

There are two main types of mica: dioctahedral micas that have only two-thirds of the octahedral cation sites occupied and trioctahedral micas that have the cation sites fully occupied. The most common dioctahedral mica is muscovite, which has an idealized composition of $K_2(Al_4)(Si_6Al_2)O_{20}(OH)_4$. Biotites are trioctahedral micas and have a formula of $K_2(Mg,Fe)_6(Si_6Al_2)O_{20}(OH)_4$, in which the relative abundance of the Fe and Mg may vary widely (Deer et al., 1962). When the trioctahedral mica contains large amounts of octahedral Fe, it is usually called lepidomelane.

The unit cells of unconstrained tetrahedral sheets tend to be larger than the unit cells of octahedral sheets. Thus, to have a combination of these sheets in one layer of a mica, their size differences have to be accommodated for by dis-

tortions in the tetrahedral sheet and/or the octahedral sheet. Tetrahedral sheets make size adjustments by rotating alternate tetrahedra clockwise and counterclockwise around the axes normal to the basal plane. These rotations not only reduce the size of the unit cell, but distort the hexagonal rings of basal oxygens into a ditrigonal arrangement (Bailey, 1966). The amount of tetrahedral rotation is primarily determined by the size of octahedra and the size of interlayer cations in the mica (Takeuchi, 1966; Franzini, 1969; McCauley and Newnham, 1971). A large rotation is found in the dioctahedral minerals that have only two of the three octahedral cation sites occupied. By comparison, octahedral sheets in trioctahedral micas require less adjustment in the size of the tetrahedral sheet. As a result, trioctahedral micas usually have several degrees less rotation than dioctahedral micas (Radoslovich and Norrish, 1962; Giese, 1979). Some variations in tetrahedral rotation also exist in micas with the same occupancy of octahedral cation sites. In addition to being rotated, tetrahedra may be tilted in some micas where large reductions in the size of the tetrahedral unit cell are needed. Thus, the tilting of tetrahedra exists primarily in dioctahedral micas.

The octahedral sheets, on the other hand, have to increase in size to articulate with the larger tetrahedral sheets. In the dioctahedral minerals, the two octahedral

cations repel each other and move farther apart while the two oxygen atoms that are shared between adjacent cations approach each other more closely. As a result, a shortening of the shared edges and a lengthening of the unshared edges of the octahedra occurs. This rearrangement of ions makes the octahedral sheets thinner and slightly larger in size.

As a consequence of the rotation of tetrahedra in mica, the interlayer K ions are not surrounded by 12 equidistant oxygens. Instead, there are six nearby oxygens and six less close oxygens around each K ion. Since the degree of tetrahedral rotation varies, the interlayer K-O distances will also vary and the bonding of interlayer K can be expected to differ with the mica. In the dioctahedral micas, the tetrahedral rotation is more pronounced, the K-O bond lengths are reduced for six oxygens and the K is bonded more strongly than it is in trioctahedral micas. When tetrahedral tilting exists, the surface oxygens of dioctahedral mica layers are not coplanar. Instead, some of the oxygens are raised 0.1-0.2 Å above the others and a corrugated surface results. Thus, the space for K between successive mica layers cannot be visualized as the space between two plane surfaces. Moreover, the corrugations of adjacent layers may or may not mesh with each other, depending on the stacking sequence and, therefore, can affect the K site in the mineral and the interlayer diffusion path K must take to be released.

The mica structure exhibits polymorphism that is prescribed by a displacement or rotations of successive layers in the stacking sequence. Smith and Yoder (1956) have shown that there can be only six mica polytypes with true periodicities of 1 to 6 layers if a single stacking angle is permitted in a given crystal. Of the theoretical mica polytypes, only certain ones seem to be common in nature (Smith and Yoder, 1956; Radoslovich, 1959; Bailey, 1966). The two-layer monoclinic ($2M_1$) polytype is the more common form for muscovite and the one-layer monoclinic form (1M) is the most common form for biotites. The stacking sequence and the regularity of this sequence affect the stability of the mica and, thereby, have an effect on the exchangeability of the interlayer K in micas.

2. Illite

The term "illite" was introduced and defined by Grim et al. (1937) as "a general term for the clay mineral constituents of argillaceous sediments belonging to the mica group." They named this material after the state of Illinois where it was found, but illites are now known to occur almost universally in sediments and soils, and are frequently interstratified. The diversity of the materials referred to as illites has caused much confusion in the literature. Even today, the Nomenclature Committee of Clay Minerals Society (1980) has not been able to accommodate illites in their

classification scheme for clay minerals.

The materials that are generally referred to as illite in the literature are 2:1 layer silicate minerals that have a structure similar to micas. Generally, two-thirds of their octahedral cation sites are occupied, as in dioctahedral micas, but they have only one-sixth of the Si in their tetrahedral layer replaced by Al. Some substitution of Al by Fe or Mg may also occur in the octahedra. This isomorphous substitution accounts for a layer charge of 130-160 meq/100 g which is primarily balanced by interlayer K, but much more Na, H, Mg, and Ca occur in illites than in micas. Chemical analyses of several illites have shown that these materials have a lower K content per unit cell and a higher interlayer water content than the micas (Gaudette et al., 1966).

Some investigators (Gaudette et al., 1966) contend that the name illite should be confined to just the nonexpanding 10 Å portion of the clay minerals in argillaceous sediments. However, it is frequently used in the literature and in this investigation in reference to mixed layer assemblages that have different amounts of contracted and expanded layers. For instance, Tumut illite is a 10 Å material that has essentially no mixed layering with expandable layers, whereas 25-30% of the layers in Grundite illite are expandable in water.

Data presented by Smith and Scott (1966) show the illites have K release characteristics that are not found in coarsely ground mica samples. More K release by layer-weathering occurs in the illites and only a limited portion of the K in illites can be replaced by Na, whereas most of the K in coarse mica particles can be extracted. Whether the mixed-layering in illites contributes to these differences has not been established but layer-weathering in fine particles of illite or ground mica seems to be involved.

3. Mica-vermiculite

For many years, the term "vermiculite" was poorly defined and was applied to any microscopic micaceous minerals that exfoliated on heating. When exfoliation occurs, the thickness of the mineral flakes may increase by 20-30 times because the layers are forced apart by an explosive release of interlayer water molecules (Walker, 1975). Chemical and X-ray investigations by Gruner (1934) led to a more precise definition of vermiculite and showed that many minerals that had previously been classed as vermiculite are really mixed layer mica-vermiculite assemblages. Therefore, Boettcher (1966) suggested that the meaning of vermiculite should be clearly defined whenever the name is used.

Vermiculites are 2:1 layer silicate minerals that have structures like micas but are expanded and have Mg in the interlayer position to balance the layer charges. The

interlayer Mg can be hydrated with as much as two layers of water molecules giving the vermiculite a 14 \AA basal spacing.

All the known vermiculite deposits have a trioctahedral structure and most of them are actually mixed layer assemblages. For example, the vermiculite deposits in Libby, Montana, are biotite, hydrobiotite and trioctahedral vermiculite mixtures (Bassett, 1959). The hydrobiotite component usually denotes a 1:1 regularly interstratified biotite-vermiculite. When a random interstratification of biotite and vermiculite or a physical mixture of biotite, hydrobiotite and vermiculite occurs, the material is generally referred to as mica-vermiculite.

Mixed-layer micaceous minerals evolve in nature through hydrothermal alterations or as a result of weathering processes that promote a partial removal of interlayer K from micas or of hydroxide interlayers from chlorite. Various experiments on the weathering of micas in laboratories have generally produced vermiculite but mixed-layer mica-vermiculite has also been produced, depending upon the severity of the method used for the extraction of K (Sawhney, 1977). By immersing biotite in $1M$ CuCl_2 solutions, for instance, Bassett (1959) produced a regularly interstratified biotite-vermiculite. He suggested that when K ions in one interlayer zone of biotite are replaced by Ca or Mg ions, the bonding in that zone becomes weaker and, as a result, bonding

in the adjacent interlayer zone becomes stronger. Hence, the next interlayer that Ca or Mg can enter is not the adjacent one, but the one beyond the adjacent interlayer, and a 1:1 regular interstratification is produced by this progressive removal of K from alternate interlayers. This concept is widely used today to explain the incomplete exchange of K that occurs in small illite and mica particles that undergo appreciable layer weathering (Scott, 1968).

4. Relevance of particle size

Due to the difficulties of obtaining uniform and pure samples of fine-grained mica, flakes of macrocrystalline micas are usually ground to obtain the material needed for particle size studies (Rich, 1970; Reichenbach and Rich, 1969; Scott, 1968). Both wet and dry grinding methods have been used to prepare these ground mica samples.

Wet grinding is usually carried out in H_2O and can result in a considerable loss of K from the mica. Lodding (1967) reported wet grinding for 90 minutes reduced the K_2O content of muscovite from 10.05 to 8.3% and grinding for 24 hours reduced it to 5.3%. Wet grinding may also cause a reduction in the silica content of muscovite (Mackenzie and Milne, 1953; Reichenbach and Rich, 1969), which means that some dissolution of the mineral occurs. Lodding (1967), on the other hand, has concluded that the silica content of the muscovite can stay essentially constant during different wet

grinding periods.

Dry grinding can raise the temperature of the mica sample to 200°C or higher and the samples can gradually be diluted with material from container and grinder (Smith and Scott, 1973). These contamination and temperature problems can be reduced by using an agate mortar, but the samples do not undergo much grinding. Another alternative is to use a water-cooled blender to prevent a rise in temperature during the dry grinding (Scott, 1968).

Grinding can have a profound effect on the exchangeability of K in micaceous materials. In a study of the effects of grinding on Grondite illite samples, Smith and Scott (1973) concluded that dry grinding converts some non-extractable K into NaCl or NaTPB extractable K by exposing interlayer K. Lodding (1970) explained his observation of an increase in extractable K in ground muscovite as being due to a release of internal strain in the mica during the grinding period, but Rich (1970) did not think an internal strain release could account for the changes in extractable K.

The sedimentation method is commonly used to separate different size fraction of particles. To make this separation, the particles must first be dispersed in water by mechanical agitation (hand shaking or high-speed blender). Ground mica samples disperse rather easily, but mechanical dispersion methods sometimes fail to break up the aggregated

particles in soil clay materials because cementing agents such as Ca and organic materials in the soil hold particles together very strongly. Therefore, various chemical additives such as NaOAc, H_2O_2 , Na-citrate, $Na_2S_2O_4$ and Na_2CO_3 , etc. are often applied to remove these cementing agents (Kilmer and Alexander, 1949; Jackson, 1958). Unfortunately, these chemical treatments can remove some of the readily exchangeable K as well and can have some effect on the exchangeability of the residual K in the illite particles (Smith and Scott, 1973).

5. Changes due to weathering

Mica weathering involves several processes, such as hydration, dissolution, hydrolysis, ion exchange and oxidation-reduction, resulting in a loss of interlayer K and/or mineral alterations that modifies the exchangeability of the interlayer K. The order in which these weathering processes occur is not always clear and the relative impact of the processes on the mineral seems to be quite variable. This subject has been reviewed in some detail by Jackson and Sherman (1953) and Loughnan (1969).

When micaceous minerals are exposed to H_2O , some hydration, hydrolysis and dissolution can be expected. The effects of hydration are particularly evident in mixed-layer minerals where some of the layers are expanded by water and more of the mineral is thereby exposed to other weathering

processes. An appreciable amount of K can be lost by micaceous minerals through hydrolysis, especially from the exposed surfaces and, thus, from the more finely divided materials and those exposed to percolating water. The exchange of H for K also produces an acidic condition on the mineral surfaces which contributes to a dissolution of the mica. Laboratory studies of the release of Si by micas in water have verified the occurrence of mica dissolution and its enhancement in minerals that have been expanded by an exchange of interlayer K.

The exchange of interlayer K by hydrated cations and the associated expansion of layer silicates constitute a major aspect of mica weathering. The changes in interlayer cations and spacings in themselves represent major alterations in the mineral, but they also change the vulnerability of the mineral to other weathering processes. Of particular interest is the concept proposed by Bassett (1959) which has the expansion of alternate interlayers causing a reduction in the exchangeability of K in the adjacent interlayers. The mixed layering arising from such a weathering process would account for the limited K release by small particles of micaceous minerals and the persistence of illites in highly weathered soils.

When the micaceous minerals contain Fe in their octahedral layers, oxidation and reduction processes can play a

major role in mineral weathering. Redox changes in the structural Fe^{++} can presumably occur prior to, during and/or after the occurrence of interlayer K exchange (Gilkes et al., 1973; Goodman and Wilson, 1973; Ismail, 1969; Scott and Youssef, 1978; Wilson, 1970). The effects of these redox changes on the mineral and on the exchangeability of interlayer K have been studied extensively in the laboratory (Kozak, 1976) and have been attributed mainly to their impact on the layer charge and structural OH orientation in the mineral (Foster, 1963; Juo and White, 1969). The general conclusion has been that structural Fe^{++} oxidation can make the interlayer K less exchangeable and the mica less vulnerable to weathering.

B. Exchangeability of Interlayer K

Considerable research has been devoted to a better understanding of the processes and factors controlling mica weathering. Since the replacement of interlayer K is one of the most important processes of this weathering, much of the research has been concerned with the exchangeability of interlayer K in micaceous minerals. Several extraction methods have been used to determine the exchangeability of the interlayer K.

1. Laboratory methods of extracting K

Salt solutions have been widely used for the extraction of interlayer K in micaceous minerals. As shown by Rausell-Colom et al. (1965), inorganic salt solutions with different cations (Na, Mg, Ca, Sr, and Ba) extract interlayer K very well. Mackintosh et al. (1971), however, used organic salt solutions (dodecylammonium chloride) to extract interlayer K and concluded that they extracted the interlayer K more effectively than the inorganic salt solutions. The effectiveness with which these inorganic or organic salt solutions work can be impaired by an accumulation of K in the extraction solutions (Hanway et al., 1957; Mackintosh et al., 1971; Rausell-Colom et al., 1965). Thus, the maintenance of a low K concentration in the extraction solution is essential when any method of extracting interlayer K in micaceous minerals is used. Reichenbach and Rich (1968, 1969) and others (Gilkes et al., 1972; Newman, 1969) renewed the extraction solution several times during the extraction period and Mortland (1958) leached mica samples with fresh increments of the extraction solution to keep the K concentration low in the extraction solutions. However, the simplest way to do so is by adding a reagent that precipitates the K as soon as it is released to the extraction solutions. When Na-cobaltinitrite was used as a K precipitant by White (1950) and Robert and Pedro (1969), they were able to extract almost all the K from

biotite samples. Sodium tetraphenylboron (NaTPB) has also been used as a K precipitant and has provided even more effective extractions of interlayer K because KTPB has lower solubility (1.8×10^{-4} mole/liter) than K-coltinitrite (2×10^{-3} mole/liter). The use of NaTPB solutions for the extraction of interlayer K was initiated by Hanway (1956) with illite. Subsequently, methods of using NaTPB solution to extract the interlayer K from various micas and illite materials have been developed by Scott and Reed (1962a,b), Smith and Scott (1966, 1974), and Reed and Scott (1961, 1966).

While the effects of dissolved K on the exchange of interlayer K by hydrated cations (Na, Ba, etc.) can be explained in terms of mass action, the same situation arises with several dissolved cations (K, NH_4 , Rb and Cs) that tend to contract the micaceous minerals. This effect, therefore, is referred to as the blocking effect of fixable cations. The level of fixable cations that can be tolerated in the extracting solution varies with the mineral. The exchange of interlayer K in dioctahedral micas is blocked by very low levels of fixable cations, whereas trioctahedral micas release K to Na solutions that contain several ppm K. As a result, the various methods that have been used to extract interlayer K have yielded a variety of results with different minerals. Fortunately, all the fixable cations form precipitates with NaTPB and their blocking of interlayer

K exchange can be minimized by using extracting solutions that contain NaTPB.

Since the exchange of interlayer K is a diffusion controlled process (Reed and Scott, 1962; Chute and Quirk, 1967), a K concentration gradient between the mineral particles and extraction solutions has to be maintained to continue the K exchange process. An accumulation of K in the extracting solution, therefore, cannot only block the exchange process but can control the rate of any exchange that does occur.

2. Role of mineral properties

The exchangeability of interlayer K in micaceous minerals depends not only on the conditions imposed by the method of extraction but on various characteristics of the micas as well. The mineral properties that are particularly relevant to K release are the mineral structure, crystal imperfections and particle size. The structural features of mica that seem to have effect on K release have been reviewed by several workers (Newman, 1969; Leonard and Weed, 1970a; Mackintosh et al., 1971; Norrish, 1972). The effects of particle size have likewise received much attention (Reichenbach and Rich, 1969; Scott, 1968), whereas the role of crystal imperfections is less well-known.

The rate at which interlayer K can be exchanged follows the order of lepidomelane > biotite > phlogopite > muscovite >

lepidolite. Norrish (1972) concluded that this order was due to the OH orientation and F content of the silicate sheet. The OH bond in the trioctahedral structures is known to be nearly perpendicular to the mica layer (Serratosa and Bradley, 1958; Bassett, 1960; Joswig, 1972; Giese, 1975), placing the hydrogen close to the interlayer cation and in a position where it reduces the K-O interaction. On the other hand, the OH groups in the dioctahedral minerals tilt away from the normal in the direction of the vacant octahedral site and make a small angle of 1.3 to 23.1° with the basal plane (Giese, 1979). Thus, the H atoms cause less shielding between the interlayer K and O atoms and the K can be held more strongly in dioctahedral than trioctahedral micas. Giese (1975) studied the interlayer bonding energy of micas and related the magnitude of this bonding energy to the OH orientation and to the repulsion between the H ion and the interlayer cation. Isomorphous substitution of F for OH occurs in some natural micas and enhances the strength with which interlayer K ions are held because the repulsive forces between the K and H ions are not present. Therefore, the exchange of interlayer K is usually difficult when the F content of the mineral is high (Bassett, 1960; Rausell-Colom et al., 1965; Newman, 1969; Mackintosh et al., 1971). Otherwise, according to Giese (1975), the exchange of F for OH has relatively little impact on the physical, chemical and

crystallographic properties of dioctahedral micas. Iron oxidation studies have also confirmed the importance of the OH orientation in micas by inducing changes in the direction of the OH bond and showing the resultant trioctahedral micas with high Fe^{+++} contents behave more like muscovite (Juo and White, 1969; Gilkes et al., 1972).

The length of K-O bond should affect the exchangeability of K in micas (Drits, 1969). In real mica structures, the tetrahedral sheets of dioctahedral micas have to make some size adjustments to fit with the octahedral sheet. This structural adjustment in the tetrahedral layer brings the interlayer K into closer contact with six of the 12 surrounded oxygens and causes a strengthening of the K-O bonds. As a result, the dioctahedral micas have K-O bonds of only 2.85 Å which are considerably smaller than the 3.00 Å bonds in trioctahedral micas where less modification in the tetrahedral sheet occurs. Thus, the K-O bond is stronger in dioctahedral micas than in trioctahedral varieties of this mineral group. This difference in K-O bond length is also responsible for the greater K exchangeability of trioctahedral micas (Drits, 1969; Brown, 1965).

When K is lost from micas, an associated positive charge is also lost and must be balanced by cation additions, oxidation of octahedral Fe^{++} and/or a substitution of hydroxyls for oxygens in the structure (Gruner, 1934). The oxidation

of structural Fe^{++} can create an asymmetric charge distribution around some of the OH groups and cause the OH dipoles to be inclined as they are in dioctahedral mica and, thereby, cause the interlayer K to be held more tightly. Fe^{++} oxidation can also occur with no change in layer charge if the mineral is deprotonated, in which case the interlayer K retention is strengthened by an elimination of the electrostatic repulsion between the H and K. Radoslovich (1963) and Giese (1971) suggested that the removal of K from some interlayers can alter the OH orientation toward adjacent interlayers and make the K in these adjacent interlayers more strongly held.

When the interlayer K is replaced by hydrated cations, an expansion of the interlayer space occurs. Such an expansion at the edges of the particles will tend to force the layers of the mica core apart and thus make the residual K more exchangeable. A decrease in the b dimension of the weathered zone of the mineral particles also occurs as K is released from dioctahedral micas (Leonard and Weed, 1967; Burns and White, 1963). Leonard and Weed (1970a) suggested that this decrease in b dimension would tend to lock the remaining K more tightly and retard its release. On the other hand, an increase in the b dimension occurs in the weathered zone of trioctahedral mica particles and can weaken or stretch the K-O bond sufficiently to enhance the exchange-

ability of the remaining interlayer K (Leonard and Weed, 1970a,b).

Various structural disorders exist in mica crystals. Surfaces exposed by mica cleavage and fractures, cracks, dislocations and vacant sites are all involved (LeRoux and Rich, 1969). Interstratification, partially opened interlayer spaces and warping of the silicate layers are also types of disorder that can be found in micas. These disorders provide sites where cations can readily exchange with the interlayer K of mica (Raman and Jackson, 1964). Rausell-Colom et al. (1965) and LeRoux et al. (1970) used an electron microprobe to study the effect of these disorders in micas and found the release of K started at the cracks, particle edges, and weathering fronts. Newman and Brown (1969) also showed that the rate of K exchange varied with the way the lateral edges were prepared. The general conclusion has been that the presence of crystal disorders such as cracks or frayed edges can enhance the rate of K exchange in mica. Raman and Jackson (1964) reported that there are openings in portions of the basal surfaces of micas which allow the layers to roll back and form scrolls. When they do so, the exchangeability of the interlayer K is increased. According to Raman and Jackson (1964), the scrolling of mica layers is enhanced by the addition of hydrated cations and reversed by an adsorption of K ions.

Since the rate of K exchange in mica is diffusion controlled, it is enhanced by a decrease in particle size because small particles have shorter diffusion paths and more lateral surface (Scott and Smith, 1967; Norrish, 1972). However, when the particles are reduced in size to the order of one micron, all the K cannot be replaced and a reduction in this maximum degree of release occurs as the particle size is reduced (Scott, 1968; Scott and Reed, 1962b; Reichenbach and Rich, 1969). This is known as the small particle effect.

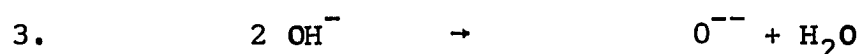
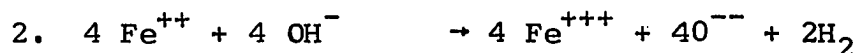
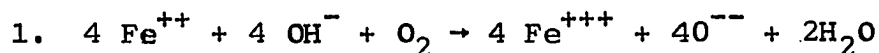
Scott (1968) determined the exchangeability of inter-layer K in several size fractions of micas and found that some of the K in mica was released immediately and this initial release of K (layer weathering) increased as the particle size decreased. The subsequent release of K (edge weathering) usually occurred at a faster rate when the particle size was decreased, but some reductions in rate were also observed. Various proposals have been advanced to explain the particle size effect, the most common being that removal of K from some layers causes it to be held more strongly in adjacent layers (Bassett, 1960; Scott, 1968; Reichenbach and Rich, 1969). However, it is doubtful that this explanation accounts for all the observed particle size effect.

C. Thermal Alteration of Micaceous Minerals

Several alterations can occur in micas as a result of heating (Brett et al., 1970; Vedder and Wilkins, 1969; Rimsaite, 1970). Particularly relevant to the exchangeability of interlayer K in the micas are those alterations that involve Fe^{++} oxidation, dehydration, dehydroxylation, deprotonation, and recrystallization. Most of these alterations occur at temperatures between 25 to 950°C, but some recrystallization may require higher temperatures.

1. Redox changes

The mechanism for Fe^{++} oxidation and an associated decomposition of structural OH groups in heated biotite has been described by Rimsaite (1970) as involving three reactions:



The reactions followed different pathways depending on the temperature, the ratio of Fe^{++} to hydroxyls in the biotite, and the presence of atmospheric O_2 . At low temperatures (450 to 650°C) in an O_2 -free atmosphere, oxidation by reaction 2 prevailed over dehydroxylation (reaction 3).

The proportion of dehydroxylation increased with increasing

temperatures to about 900°C. When O₂ was available, Fe⁺⁺ in biotite was oxidized by reaction 1, and the mica lost OH as H₂O. Hogg and Meads (1975) studied the thermal decomposition of biotite by using Mössbauer measurements and found substantial oxidation of Fe⁺⁺ took place at temperatures below 400°C, while dehydroxylation occurred at slightly higher temperatures.

2. Dehydroxylation

Dehydroxylation is the process by which minerals lose their structural OH groups. There are two mechanisms by which dehydroxylation can occur (Taylor, 1962). The homogeneous mechanism involves a direct interaction between the OH groups of octahedral layers to form H₂O. It commences at the outer edge of the mineral and advances toward the center of the crystal. The inhomogeneous mechanism proposed that the reaction takes place simultaneously throughout the bulk of the crystal. The homogeneous mechanism has been favored by most of the workers (Rouxhet, 1970; Vedder and Wilkins, 1969; Wardle and Brindley, 1972; Heller-Kallai and Rozenon, 1980).

Trioctahedral micas that are Mg rich generally lose structural OH at higher temperatures than their dioctahedral analogues. Wardle and Brindley (1972) suggested that this difference in dehydroxylation temperatures is due to less freedom for cations and oxygens to move and, thereby, re-

organize the structure of trioctahedral minerals. In muscovite, dehydroxylation can take place over a wide range of temperatures, the large well-crystallized sheets being resistant to thermal decomposition unless the temperatures are well above 500°C, while finely divided muscovite begins to lose its structural OH at an appreciable rate at temperatures as low as 400°C (Gaines and Vedder, 1964; Roy, 1949). Kodama and Brydon (1968) have also observed that dehydroxylation occurs at progressively lower temperatures as the particle size is reduced.

Sayin and Reichenbach (1978) heated 2-5 μm muscovite samples for 1 hour at temperatures that were increased from 300 to 1000°C by 100°C intervals and examined the mineral for structural changes by infrared and X-ray diffraction measurements. They reported the structure of muscovite starts losing OH ions at 500°C as evidenced by intensity decreases in the OH-stretching vibration at 3638 cm^{-1} and the OH libration motion at 928 cm^{-1} .

At 600°C, the OH libration disappeared but the OH stretching persisted until the samples were heated at 800°C and the IR bands showed almost no changes at temperatures higher than 800°C.

The kinetics of dehydroxylation has been investigated by Gaines and Vedder (1964), Vedder and Wilkins (1969), and Rouxhet (1970). The primary step in the dehydroxylation of

muscovite appears to be the formation of H_2O molecules. The concentration of these H_2O molecules tends to build up in the mica layer to a temperature-dependent equilibrium value. Loss of the H_2O by a diffusion of H_2O molecules through the mica layer can occur but can be the factor that limits dehydroxylation in muscovite at temperatures below approximately $650^{\circ}C$. At about $700^{\circ}C$, however, the concentration of H_2O molecules inside a thick sheet of muscovite may reach a point where the pressure is sufficient to produce delamination, subsequently reducing the diffusion distance and correspondingly accelerating the loss of H_2O . With finely divided samples, the pressure needed for delamination does not build up, and diffusion remains the controlling step over a wider range of temperatures. Kodama and Brydon (1968) have reported that the rate of dehydroxylation in microcrystalline muscovite can be controlled by a two-dimensional diffusion process in the reaction product. Their results support the concept that dehydroxylation involves a homogeneous decomposition mechanism. By studying the kinetics of dehydroxylation in macrocrystalline micas, Rouxhet (1970) decided that dehydroxylation can occur by the diffusion of either OH or H_2O groups through the mica layers.

3. Structure modifications

Eberhart (1963) proposed a homogeneous dehydroxylation mechanism for heated muscovite. By this mechanism, neighboring pairs of OH groups interact to form a H_2O molecule and the leftover oxygen ions occupy the vacant octahedral sites. Wardle and Brindley (1972) investigated the structure of dehydroxylated pyrophyllite and reported that the residual oxygen ions from the dehydroxylation remain in the layer structure and are located midway between the original OH sites in the same plane as the octahedral Al cation. Dehydroxylation of pyrophyllite caused an increase in the a and b dimension of the mineral; thus, an untwisting of tetrahedra must occur to reorganize the octahedral sheets (Brindley, 1971). Wardle and Brindley (1972) indicated that the expansion of the octahedral sheet arises largely from the rearrangement of the Al ions and the insertion of oxygen ions in the Al plane. By using a one-dimension Fourier synthesis with heated muscovite (Eberhart, 1963) and heated pyrophyllite (Wardle and Brindley, 1972), it has been shown that the electron densities of the Al plane are higher in the dehydroxylated phase than those in the original minerals. Sayin and Reichenbach (1978) interpreted these changes in electron density as being due to a movement of residual oxygen ions to the level of Al ions.

Vedder and Wilkins (1969) and Eberhart (1963, 1964)

observed increases in all the unit cell dimensions of dehydroxylated muscovite. The relative increase along the c and b axes was considerably greater than the increase along the a axis. According to Eberhart (1963, 1964), these increases are the net result of several structural alterations that involve changes in the thickness of the sheets, tetrahedra rotations, etc. Sayin and Reichenbach (1978) compared the X-ray diffraction patterns of heated and unheated samples of 2-5 μm muscovite and found the heat treatment caused an increase in both the c and the b dimensions of the mineral. The c dimension increased from $9.99 \pm 0.1 \text{ \AA}$ in the original muscovite to $10.08 \pm 0.01 \text{ \AA}$ in 700°C-heated samples, whereas the b dimension increased from $8.98 \pm 0.02 \text{ \AA}$ to $9.09 \pm 0.02 \text{ \AA}$ in 600°C-heated samples. These unit cell dimensions remained the same when higher heating temperatures were used. It was evident from the X-ray patterns, however, that heating temperatures above 700°C did cause some alterations in the mineral because the high order reflections were increased relative to the first order reflection.

Illite and montmorillonite (Grim and Bradley, 1940), kaolinite (Brindley and Gibbon, 1968) and pyrophyllite (Wardle and Brindley, 1972) are other dioctahedral layer silicates that have been expanded in the c direction by heating.

The trioctahedral micas, on the other hand, exhibit a decrease in their c dimension when they are heated (Drits, 1969). From work with biotite, Wones (1963) suggested that oxidizing the structural Fe^{++} ions to smaller Fe^{+++} ions (0.83 \AA compared to 0.67 \AA in radius) would shrink the octahedral sheet and force the tetrahedral sheet into greater ditrigonal distortion. Wones showed the a, b and c dimensions of biotite all decreased when the oxybiotite content increased. Rimsaite (1967) heated several biotites and found the heat treatments produced distinct reductions in the d(001) and d(010) spacings which correlated with the degrees of Fe^{++} oxidation. However, Takeda and Morosin (1975) found all the cell dimensions increased in a heated sample of synthetic fluorphlogopite which contained no Fe^{++} .

4. Effect on K exchangeability

The exchangeability of interlayer K in mica depends, to some extent, on the abundance of OH groups and the orientation of the OH dipoles in mica. Consequently, any thermal alteration of mica that involves these OH groups will also change their K exchangeability.

Dehydroxylation causes a structural rearrangement in the mineral and, thereby, a change in the dimensions of the mineral. In heated dioctahedral micas, increases in the c dimension (Vedder and Wilkins, 1969) render the interlayer K

more accessible to exchange and increases in the b dimension weaken or stretch the K-O bond sufficiently to enhance K release (Tomita, 1974). Trioctahedral micas, on the other hand, tend to contract its cell dimensions when heated (Wones, 1963; Drits, 1969) and the K exchange becomes more difficult. Scott et al. (1972) determined the exchangeability of K in several heated mica samples and found the maximum degree of K exchange was generally unaltered by the heat treatments, but the rate of K exchange underwent major changes in biotite, lepidomelane, and muscovite samples. The rate of K release was enhanced in heated muscovite, whereas, the rate was retarded in heated biotite and lepidomelane. When Grondite illite samples were heated at 450°C for 24 hours, Smith and Scott (1963) found the maximum extractable K was increased substantially. This heat treatment also increases the initial release of K by layer weathering and the maximum degree of K release by several fine-grained micaceous minerals (Smith and Scott, 1974).

Ferrous iron oxidation causes a loss of layer charge and leaves the interlayer K in a more negative environment. This oxidation also causes alterations in the orientation of structural OH groups making K exchange more difficult in high Fe trioctahedral micas (Juo and White, 1969; Gilkes et al., 1972). Robert and Pedro (1968, 1969) and Robert (1971) have observed with heated biotite samples that both

the rate and the degree of K release can be reduced when Fe^{++} in the mineral is oxidized. However, Smith and Scott (1974) concluded that Fe^{++} oxidation does not always impair the exchangeability of interlayer K because they observed increases or no change in maximum K release in heated samples of fine-grained micaceous minerals that contained structural Fe^{++} .

III. MATERIALS AND METHODS

A. Mineral Samples

One muscovite, two illites and four mica-vermiculite samples were ground and/or fractionated to obtain samples with different particle sizes for this study.

Large crystalline sheets of muscovite from Keystone, South Dakota, were obtained from Wards Nature Science Establishment Inc., Rochester, New York. These sheets were sorted, and those free of visible impurities were broken up by hand, coarsely ground in a Wiley Mill and then more finely ground in a shatterbox with a tungsten carbide grinder. Due to the high yield of very fine particles ($<2\text{ }\mu\text{m}$) in the shatterbox, part of the muscovite was ground less finely in a Waring Blendor with a water-cooled, stainless steel container that kept the temperature of the minerals below 60°C . The ground muscovite was suspended in water to separate, 10-20, 5-10, 2-5, 0.2-2 and $<2\text{ }\mu\text{m}$ fractions by sedimentation. Each size fraction was concentrated in auto-irrigator pots, air dried and crushed to pass a 60-mesh screen.

Grundite illite from the Goose Lake area, Illinois, was obtained from the Illinois Clay Products Company. Air-dry chunks of Tumut illite from Tumut, New South Wales, Australia, were obtained from Dr. K. Norrish, CSIRO, Adelaide, Australia. These illite samples were first

suspended in water by hand shaking and the $<2\ \mu\text{m}$ fraction was separated by sedimentation. The coarse residue was then dispersed with a Waring Blendor and sedimented again to separate $<2\ \mu\text{m}$ particles. The combined $<2\ \mu\text{m}$ suspensions of each illite were concentrated in auto-irrigator pots, air dried and crushed to pass a 60-mesh screen.

The four mica-vermiculite samples came from specific site locations in commercial vermiculite mines. Due to their high content of K and $10\ \text{\AA}$ mica layers, however, they cannot be called vermiculites (Walker, 1975). Instead, they are coarse-grained mixtures of trioctahedral vermiculite, biotite and hydrobiotite (a 1:1 regularly interstratified 10:14 \AA component). Two of these mica-vermiculite samples came from a mine at Greenville, South Carolina, the other two from a mine at Libby, Montana and all were supplied by the Zonolite Company. The two samples from each mine were distinguished by having a high or low cation exchange capacity, a difference that stems from the presence of few or many $10\ \text{\AA}$ mica layers, respectively. Therefore, these four mixed-layer samples will be referred to as South Carolina high (SCH), South Carolina low (SCL), Montana high (MH) and Montana low (ML) minerals. Each of these mineral samples was crushed in a hammer-mill to pass a 1/16-inch screen on the mill. These samples were not suspended or washed in water and were not subdivided in any way.

Total K determinations were carried out with all the mineral samples and showed there was 216, 211, 209, 204, 201 meq K/100 g in the 10-20, 5-10, 2-5, 0.2-2 and <2 μm fractions of muscovite, 203 and 116 meq K/100g in the <2 μm Tumut and Grundite samples and 55, 107, 75 and 197 meq K/100 g in the SCH, SCL, MH and ML samples, respectively. Fe^{++} determinations showed there was 11, 17, 11 and 91 mmoles Fe^{++} /100 g in the SCH, SCL, MH and ML samples, respectively. The other mineral samples contained minor amounts of Fe^{++} , except the <2 μm Grundite illite, which contained 38 mmoles Fe^{++} /100 g.

B. Thermal Treatments

Portions of each mineral sample were heated for different periods in a regular drying oven at 110 and 200°C and at temperatures from 250 to 950°C in a Lindberg Hevi-Duty muffle furnace that was equipped with a digital controller capable of controlling temperatures to better than $\pm 1^\circ\text{C}$. The various heat treatments were carried out with weighed 0.5 g samples (110°C, 24-hour, oven-dry basis) of air-dry mineral in platinum crucibles. The samples were placed on a raised platform in the oven or furnace, heated for the prescribed period and cooled in a dry desiccator. The heated samples were then weighed to determine how much weight was lost during the heat treatment and used in

exchangeable K or other mineral property studies.

A few 0.5 g mineral samples were heated at temperatures of 110 to 500°C while enclosed in a Parr pressure bomb with enough H₂O to provide a H₂O-saturated atmosphere. The bomb had a capacity of 71 ml and was constructed of inconel 600 to withstand a pressure of 6000 psig at 600°C. By using 7.2 ml of added H₂O and a maximum temperature of 500°C, these heating experiments were carried out with plenty of margin for safety. Two mineral samples in open platinum thimbles were heated at one time and no weight loss determinations were made as H₂O condensed on the samples during the cooling period.

C. Potassium Extraction

A method of extracting interlayer K from micas with NaCl-NaTPB-EDTA solutions has been developed by Scott and Reed (1962a, 1962b), Reed and Scott (1966), and Smith and Scott (1966). Their general procedure was used to determine the exchangeability of the interlayer K in the various mineral samples after they were exposed to different heat treatments. The K extractions were carried out by mixing the entire 0.5 g heated samples with 0.684 g NaTPB powder, adding 10 ml 1N NaCl-0.01M EDTA solution and storing the mixtures for different periods at 25°C. When the extraction period did not exceed 30 minutes, the NaTPB was dissolved

in the NaCl-EDTA solutions and the 0.5 g samples were added last to prevent problems from the NaTPB dissolution period.

The K extraction process was terminated after specified contact periods by adding 18 ml of 2N NH_4Cl blocking further K release and subsequent K reversion. The samples were then transferred to 1-liter flasks containing 10 ml 0.2N CuCl_2 solution, the solution volumes were increased to approximately 70 ml with H_2O and the mixtures were boiled on a hot plate until all the precipitated K (KTPB) was brought into solution. The solutions were filtered while still warm and the filtrates were collected in a flask containing 5 ml 1N HCl to prevent precipitation of copper. The mineral residues were leached with 7 ml 2N NH_4Cl solution and the filtrates were diluted to 100 ml by adding water.

D. Chemical and XRD Analyses

The total K analyses were carried out by using the HF-HClO_4 digestion method described by Jackson (1958) and determining the K in the digest with a Baird-Atomic Inc. model KY-2 flame photometer and 100 ppm lithium as an internal standard. The NaCl-NaTPB extracted K was determined with the same flame photometer.

Ferrous iron determinations were carried out with weighed portions of the heated mineral samples and the

method described by Peters (1968). Instead of diphenylamine, however, the Na salt of p-diphenylamine sulfonic acid was used as the indicator. The indicator was prepared by dissolving 0.1 g of the Na salt of p-diphenylamine sulfonic acid in 100 ml of concentrated sulfuric acid. In general, 8 drops of indicator solution was sufficient for adequate color development.

The results of all chemical analyses and weight loss determinations were expressed in terms of the 100°C, 24-hour, oven-dry weight of the mineral sample.

X-ray diffraction (XRD) patterns were obtained with oriented specimens of heated and unheated minerals on ceramic tiles. The oriented specimens were prepared by placing a H₂O slurry of the mineral sample on a ceramic tile, removing the excess H₂O by suction and allowing the samples to air dry. A Hilgar Watts diffractometer and Ni filtered Cu radiation were used for the XRD analyses. Corundum was mixed with the mineral samples when an internal standard was needed to test for small changes in the basal spacing of the micaceous minerals.

IV. RESULTS AND DISCUSSION

The fact that the K release behavior of micaceous minerals can be altered by heating the mineral was established some time ago with Grundite illite samples (Smith and Scott, 1963). Further experiments with many other micaceous minerals have shown that these thermal alterations in K exchangeability vary with the mineral and, thereby, offer a way of assessing the mineral parameters that govern K release. This concept was developed in general by Scott et al. (1972) and pursued more specifically with ground muscovite and lepidomelane by Kozak (1976).

Major reductions in K release rates have been observed in heated trioctahedral micas and have been readily accounted for by the oxidation of structural Fe^{++} and associated changes in OH orientation that occur with heating. The dioctahedral micas, on the other hand, have exhibited complex changes in K release that have not been fully explained. Using $<50 \mu\text{m}$ samples of Effingham muscovite, Kozak (1976) showed that rates of K release can be increased or decreased by thermal treatments. The increases in release rate were attributed to the occurrence of dehydroxylation and changes in $d(001)$ spacing in the heated muscovite, whereas, no mineral property could be related to the decrease in K release rate. It was concluded, therefore, that this investigation should focus on the effects of thermal treatments on the exchangeability

of K in dioctahedral micaceous minerals.

Noting that the initial segment of exchangeable K in <50 μm muscovite samples gave the quickest response to thermal treatments and exhibited both increases and decreases in release rate at temperatures that only increased the release rate of the rest of the K, Kozak (1976) questioned whether some very fine mica particles in this sample (which would contribute most of the initial K release) were giving thermal responses ahead of the coarser particles. To test this possibility, he carried out preliminary experiments with heated samples of 10-20 μm Keystone muscovite. A similar complex combination of increases and decreases in K release rate were observed and no evidence of major differences due to fine particles in the <50 μm mica samples were obtained. Nevertheless, this approach of using mineral samples with a defined range of particle size was adopted for this study and was extended to compare ground mica samples of different sizes and ground versus naturally occurring particles of the same size.

Using the same 10-20 μm sample of ground Keystone muscovite as Kozak (1976), the effects of heat treatments on the exchangeability of K in coarse-grained mica particles were first examined in some detail. Various size-fractions of ground Keystone muscovite were then compared in terms of their susceptibility to thermal alterations. One of these

ground mica samples was a $<2\ \mu\text{m}$ fraction which served as a reference in a subsequent determination of the changes in K exchangeability in heated samples of naturally occurring $<2\ \mu\text{m}$ size-fractions of Tumut and Grundite illites. Attention in this comparison of $<2\ \mu\text{m}$ samples was directed at the effects grinding (muscovite versus Tumut illite) and mixed layering (Tumut versus Grundite illite) might have on thermally induced changes in K exchangeability. All the muscovite and illite samples were dioctahedral minerals and were expected to differ from trioctahedral micas by yielding an increase in K release rate with some heat treatments. In a survey of the K release behavior of a variety of heated micaceous minerals, however, Scott et al. (1972) encountered a trioctahedral mica-vermiculite that behaved like the dioctahedral minerals in that its K release rate was increased by heat treatments. Thus, this mica-vermiculite was incorporated in this study of predominately dioctahedral minerals and compared with other mica-vermiculites that had different degrees of mixed layering. One of these mica-vermiculites was essentially biotite. Therefore, it was anticipated that this group of mica-vermiculites might yield thermal responses that ranged from those observed with dioctahedral minerals to those of trioctahedral minerals.

Portions of each mineral sample were heated in an oven or a furnace at different temperatures and for different

periods. Most of these heated samples were then placed in NaCl-NaTPB solutions at 25°C for specified periods to determine the exchangeability of their interlayer K. Other heated samples were examined for thermal alterations by X-ray diffraction analyses. In either event, the mineral samples were weighed before and after each heat treatment to determine their weight loss.

A. Coarse-grained Muscovite

The curves in Fig. 1 describe the K release behavior of the 10-20 μm Keystone muscovite samples that were heated for specific periods at selected temperatures. The curves for the 600°C, 2-week; 800°C, 1-hour; and 800°C, 12-hour treatments were obtained earlier by Kozak (1976) and are included here without data points to provide references for the data obtained with other heat treatments.

In earlier experiments with 10-20 μm Keystone muscovite, Kozak (1976) used a minimum heating temperature of 600°C and found the rate of K release increased progressively as the heating period was increased to 2 weeks. By contrast, the 350°C, 24-hour treatment in this study retarded the rate of K release. Moreover, the maximum degree of K release was less in the 350°C-heated samples than it was in the unheated or 600°C-heated mica. As shown in Fig. 1, an increase in the heating temperature from 600 to 800°C or 900°C also

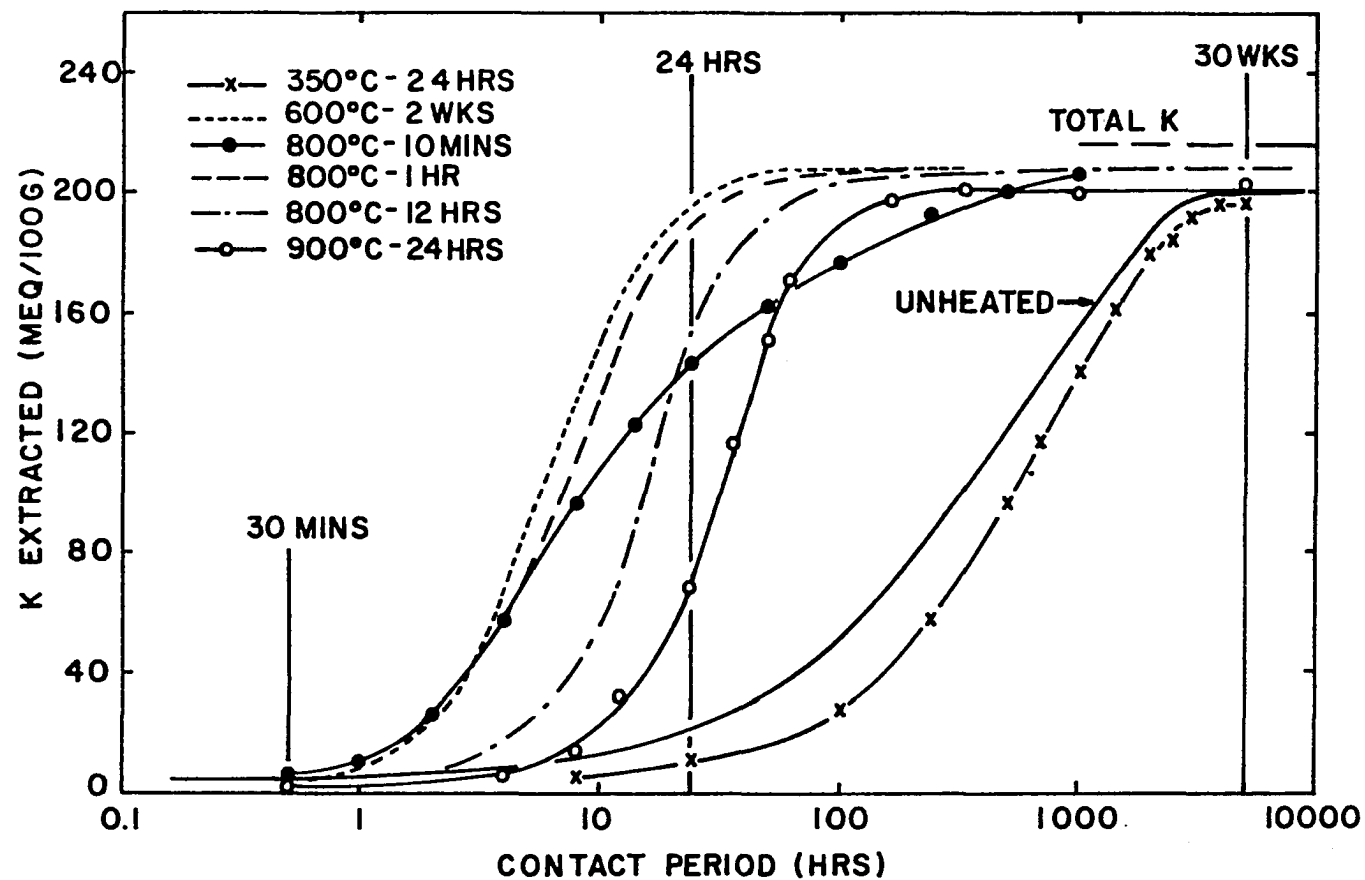


Fig. 1. K extracted from 10-20 μ m muscovite samples that were heated at different temperatures for different periods and then placed in NaCl-NaTPB solutions for different periods

reduced the rate of K release and sometimes the maximum degree of K release. These effects of high heating temperatures are obviously complicated by the length of the heating period. Samples heated at 800°C for only 10 minutes released a portion of their K as rapidly as the 600°C, 2-week and 800°C, 1-hour samples, but the rest of the K was released at a slower rate. Based on Kozak's observations with samples heated at 600°C for different periods, the 15 minute treatment was not long enough to maximize the release rate of K from all parts of the mica particles; that is, portions of the mica particles that were heated for 10 minutes were not completely altered by a temperature of 800°C. Overall, the data in Fig. 1 make it clear that detailed studies of the effects of many temperatures and heating periods would have to be made to describe the complex nature of the associated changes in K exchangeability. For such studies, it was not feasible to determine the entire K extraction curve for every thermal treatment. Instead, K extraction periods of 30 minutes, 24 hours and 30 weeks were used to determine the effects of the thermal treatments on the initial K release, the rate of K release and the maximum degree of K release, respectively. The particular portion of the K extraction curve that is described by these extraction periods is identified in Fig. 1.

A detailed study of the changes that occur in heated

muscovite was initiated with a determination of the effects imposed by different temperatures. To do so, samples of 10-20 μm muscovite were heated for 24 hours at many different temperatures and then placed in NaCl-NaTPB solutions for the three extraction periods. The weight of each mica sample was determined before and after the heat treatments to measure the dehydration and dehydroxylation that occurred during the heating period. The curves in Fig. 2 describe the changes in K exchangeability and sample weight that were observed when the heating temperature was varied.

The K release curves for the 30-minute and 30-week extraction periods make it clear that heating temperatures up to 900°C had little effect on the initial and maximum amounts of K released by 10-20 μm muscovite. This means there was no change in the tendency for these mica particles to undergo layer weathering and no evidence of K being made inaccessible to exchange by a recrystallization of the mineral at even the highest temperatures. On the other hand, the 24-hour K curve shows the rate of K release underwent substantial changes when the heating temperature was increased. The amount of K released in 24 hours actually decreased when the temperature was increased to 350°C but then increased to a maximum near 700°C before it decreased again with higher temperatures. These results reiterate in greater detail the observations already made in regard to Fig. 1

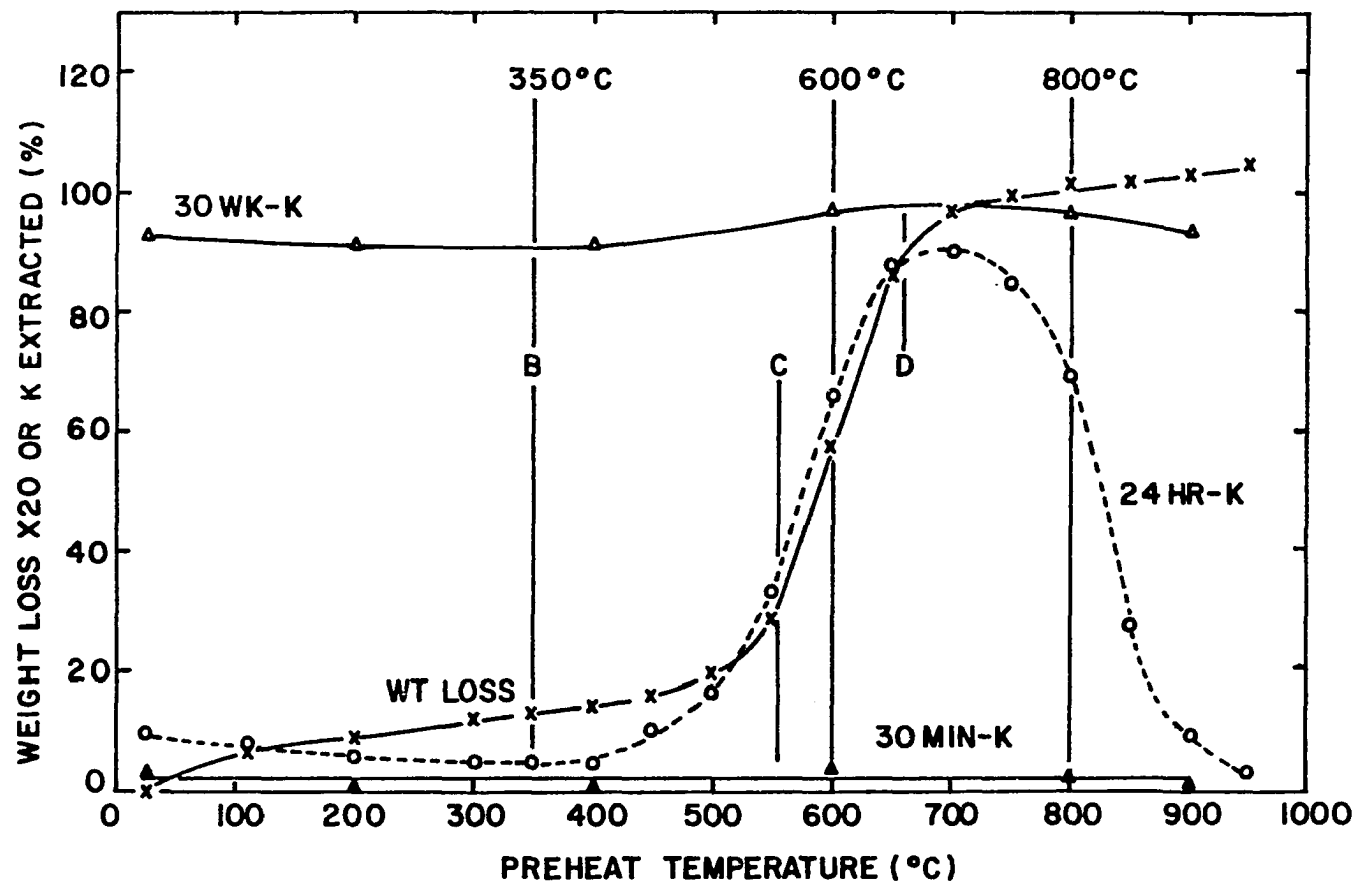


Fig. 2. Weight loss by 10-20 μ m muscovite samples that were heated at different temperatures for 24 hours and K extracted by placing the heated samples in NaCl-NaTPB solutions for 30 minutes, 24 hours, and 30 weeks

that heated muscovite undergoes changes that retard, enhance and then retard the rate of K release when the intensity of the thermal treatment is increased.

A comparison of the 24-hour, K release curve and the weight loss curve in Fig. 2 suggests that some of the changes in K release rate may be related to the weight losses in the heated mica. The samples heated at temperatures up to 350°C exhibited a loss in weight that can be attributed mainly to dehydration. Even though this loss of water increased as the K release rate decreased, it is hard to conceive of a way the removal of water that is primarily on the surfaces of the particles could affect the release of more than just the initial increments of K. Major increases in weight loss and release rate occurred when the heating temperature was increased from 500 to 700°C. In this temperature range, dehydroxylation accounted for most of the weight loss in the heated mica and could have been involved in the parallel increase in K release rate because the mineral structure is altered by a loss of structural OH groups. Increases in the temperature beyond 700°C enhanced the loss of weight but reduced the K release rate. Both of these high temperature changes could be accounted for rather easily by a recrystallization of the mineral. However, as noted earlier, the consistency of the maximum K release values that were obtained with all the heated samples refutes

this possibility of recrystallization. Thus, by themselves, the data in Fig. 2 left many aspects of the weight loss - K release relationship unresolved.

A heating period of 24 hours was used to determine the effects of different heating temperatures on the exchangeability of K in 10-20 μm muscovite. It was anticipated that changes in the heating period would also affect the K release behavior of the mica. Thus, experiments were carried out with samples that were heated at 350, 600 and 800°C for different periods and then extracted with NaCl-NaTPB solutions for 24 hours. The K release and weight loss results from these experiments are presented in Fig. 3 and 4, respectively.

The K release and weight loss values were not affected by the length of the heating periods at 350°C, whereas they both increased progressively when the heating period was increased from 10 minutes to 2 weeks in the 600°C experiment. The K release and weight loss that occurred in the 800°C-heated samples increased with the heating period until a period of 1.5 hours was reached; thereafter, the weight loss was relatively constant while the K release decreased rapidly as the heating period increased. Thus, these experiments verified the importance of heating the mica for specified periods to obtain particular degrees of mica alteration. Some of the changes in K release and weight loss that were

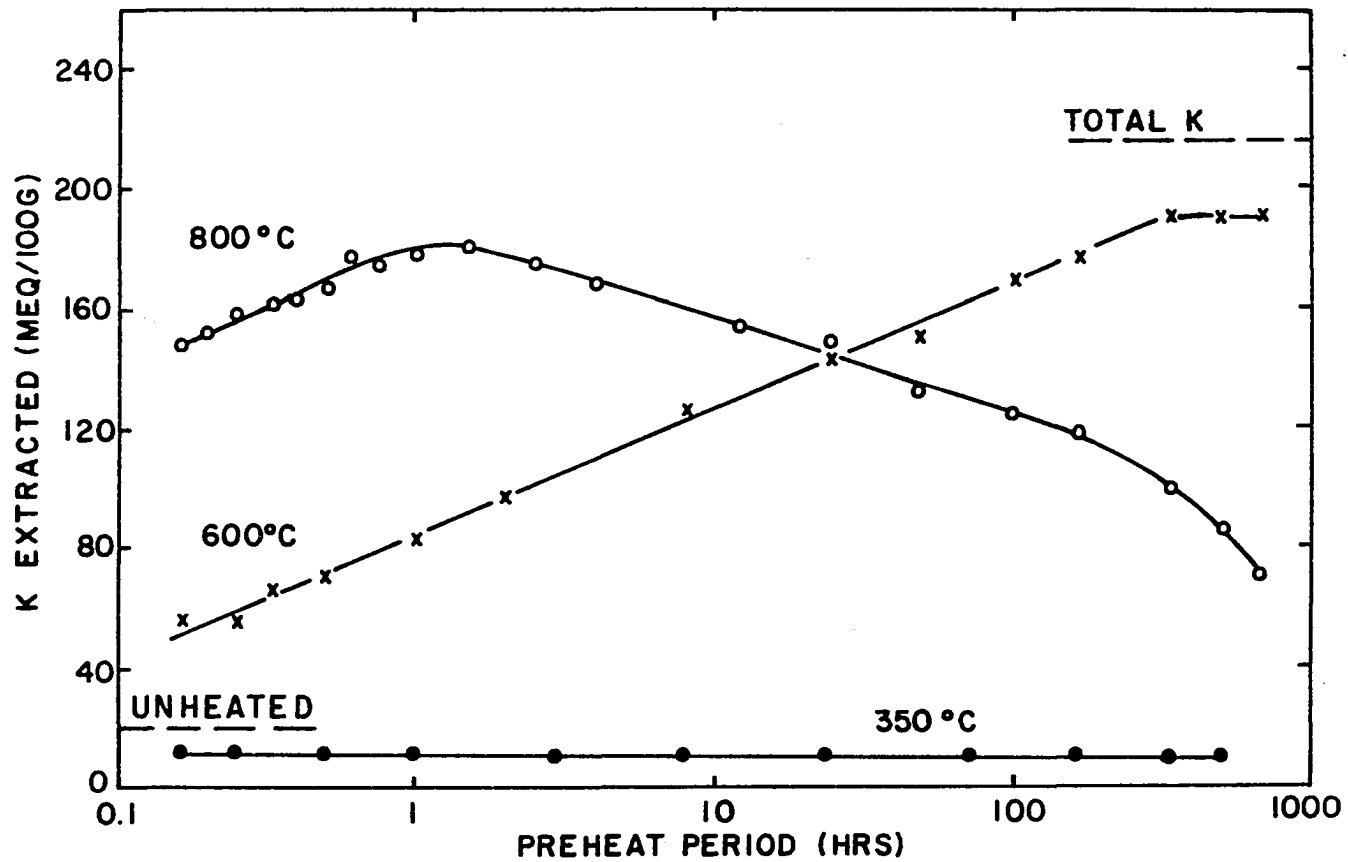


Fig. 3. Effect of heating periods on the K extracted from 10-20 μ m muscovite samples that were heated at different temperatures and then placed in NaCl-NaTPB solutions for 24 hours

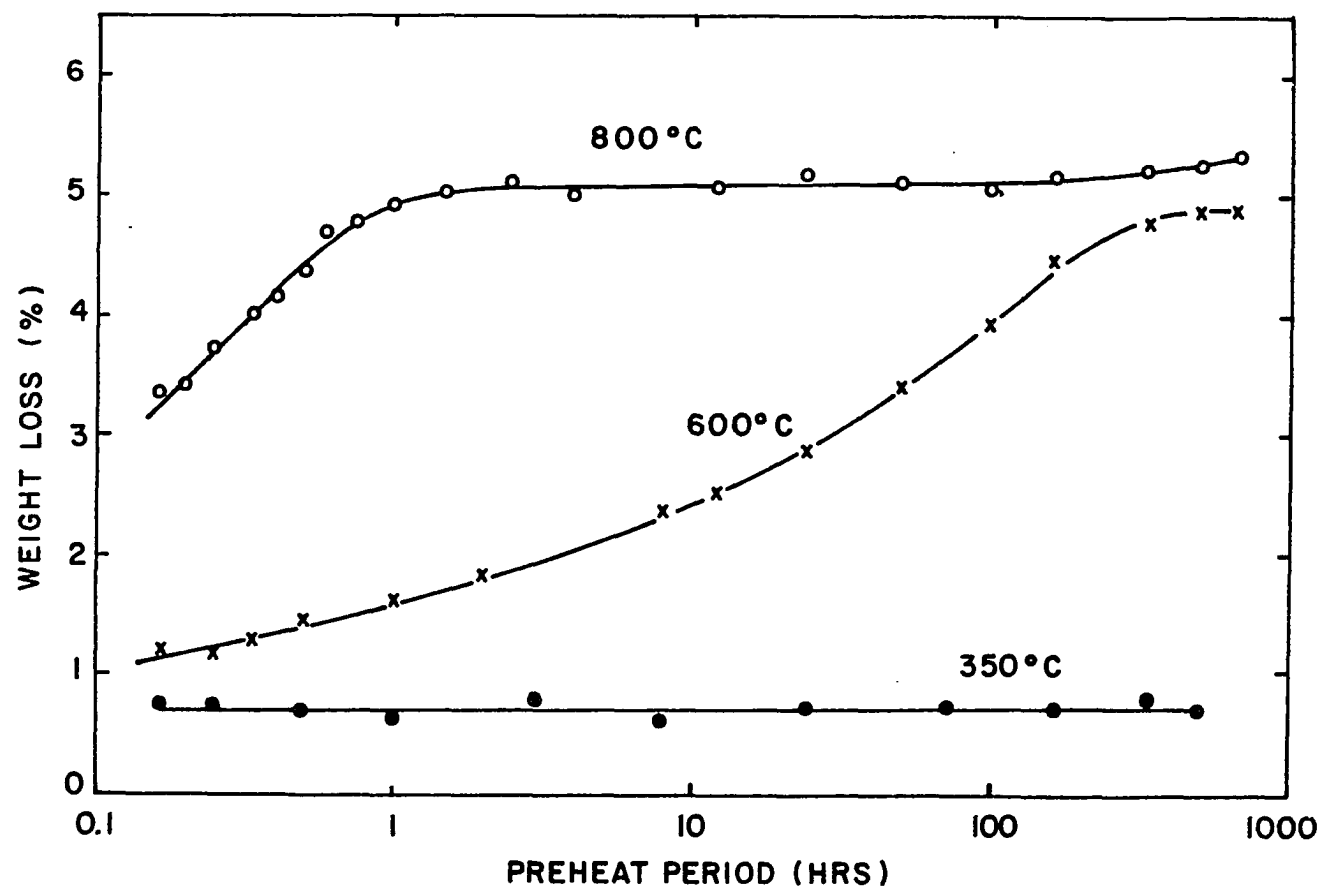


Fig. 4. Weight loss by 10-20 μm muscovite samples that were heated at different temperatures for different periods

induced by different periods were also shown to be related; that is, the K release rate increased when the mica samples lost weight, presumably by dehydroxylation, at temperatures of 600 and 800°C. On the other hand, the data obtained with samples that were heated at 350°C or at 800°C for periods over 1.5 hours are more confusing. While the heat treatments at 350°C reduced the K release rate, the degree of this effect was the same when heating periods of 10 minutes or 3 weeks were used. Since the weight loss did not change with the heating period at 350°C either, a relationship between this weight loss and the decrease of K release rate cannot be ruled out, but it is clear that both changes occurred in less than 10 minutes. Even more important is the observation from the 800°C experiment that reductions in K release rate can occur in heated mica even though no loss of water (weight loss) occurs. Under this intensity of heating, at least the mica must undergo alterations other than water loss that are enhanced by an extension of the heating period and are somehow involved in the K release process.

The preceding experiments on the effects of different heating temperatures and heating periods on the exchangeability of K in 10-20 μm muscovite samples provided some indication that a relationship between these effects and the mineral weight loss might exist. Thus, additional experiments

were carried out with a variety of heating temperatures and periods that produced different degrees of weight loss in the muscovite samples. Extraction periods of 24 hours were used to determine the rate of K release in each sample. These K release results were combined with data from the preceding experiments and plotted in Fig. 5 to show their relationship to the weight loss that occurred in the same heated samples.

Several changes in the rate of K release occurred when the weight of the mineral sample was progressively reduced by thermal treatments. The release rate first decreased from level a to b, but it then increased as the weight loss increased and finally decreased again as the weight loss approached a maximum. Only one of these three changes in the exchangeability of K in heated muscovite, however, appears to be closely linked with the thermally induced weight loss. Over the CD section of the curve, the release rate increased in direct proportion with the weight loss. From the shape of the weight loss curve in Fig. 2, it can be assumed that the weight loss from C to D was due to dehydroxylation in the mineral. Thus, this CD portion of the change in K exchangeability can be attributed to mineral alterations that involve a loss of structural water. In similar studies with $<50\text{ }\mu\text{m}$ muscovite samples, Kozak (1976) related this increase in K exchangeability to measured in-

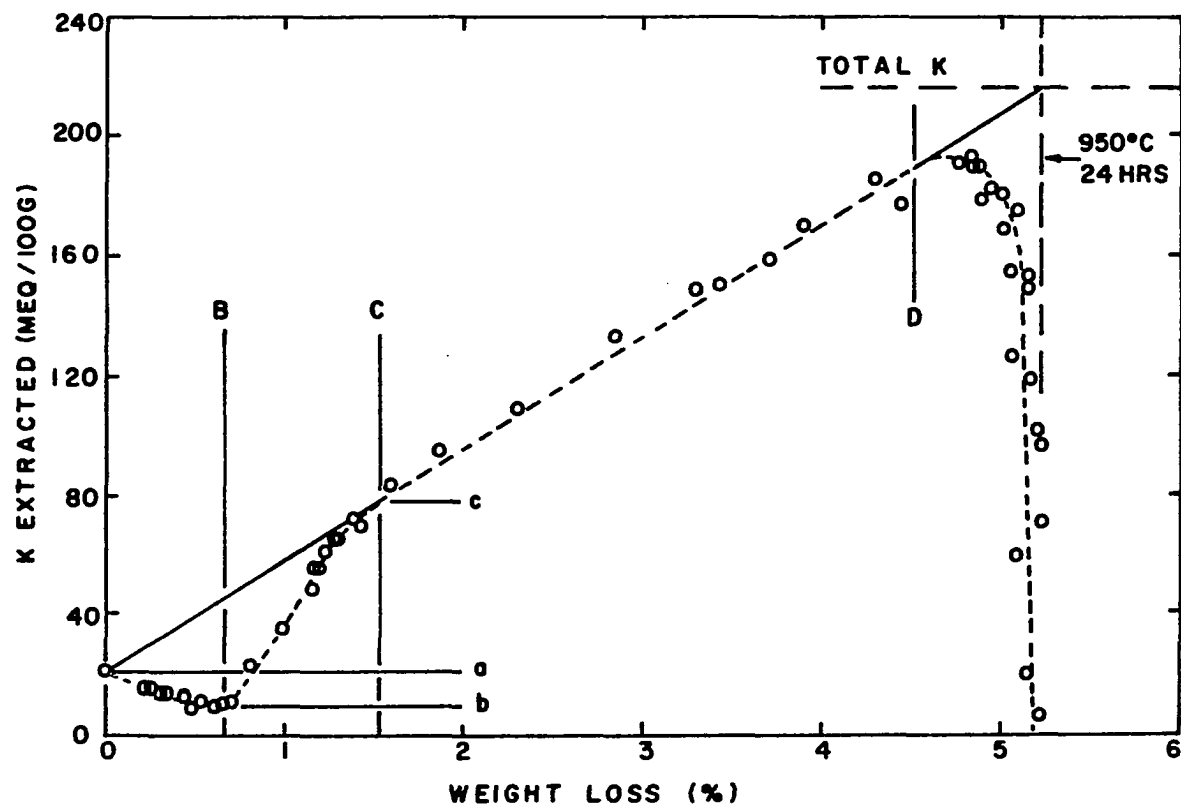


Fig. 5. Relationship between the K released by heated 10-20 μ m muscovite samples in NaCl-NaTPB solutions for 24 hours and the mica weight loss during the heat treatments

creases in the $d(001)$ of the heated mica but it was also noted that the dehydroxylation process leaves residual oxygen ions that move away from the interlayer K and leave the K in a more exchangeable site.

The decrease in K release rate in Fig. 5 cannot be explained in terms of the weight loss in the heated mica. Once the mica was dehydroxylated, the rate of K release decreased dramatically while the weight loss changed only slightly. Thus, another mineral alteration must have occurred in the heated samples of dehydroxylated mica. Structural rearrangements that lead to a reduction in the interlayer space seem to be the most likely possibility since recrystallization has been ruled out by the complete exchange of K shown in Fig. 2 for 900°C-heated muscovite. X-ray diffraction analyses of several samples of dehydroxylated mica that had been heated enough to reduce the K release rate to different degrees, however, did not produce any evidence of a decrease in the basal spacing of the mineral. This does not mean, of course, that changes in the interlayer spacing did not occur because the changes needed to reduce the K exchangeability could be too small to measure. The basal spacing increased less than 0.1 Å during the dehydroxylation of the mica but even this change was not reversed by more intensive heating. Some structural changes must have occurred in the muscovite samples that had reduced K release rates because

the high order X-ray reflections increased relative to the first order reflections as the heating temperatures and periods were increased. Perhaps the interlayer spacing did decrease but was compensated for by other structural changes that left the measured $d(001)$ constant.

The changes in K release rate that occurred with the initial 1.5% weight loss are complex and indicative of the presence of more than one thermal effect. The onset of dehydroxylation probably overshadowed the process that reduced the rate from a to b, but why the release rate increased so sharply from b to c instead of reflecting the changes described by the CD segment of the curve is not clear. All these changes occurred with muscovite samples that were heated just enough to cause mainly dehydration. Thus, to determine whether the hydration water in muscovite had any effect on the rate of K release, experiments were carried out with 10-20 μm samples that were heated for specified periods at several low temperatures and were then rewetted with water or steam before they were placed in NaCl-NaTPB solutions to extract K. Table 1 lists the weight loss that occurred in the heated samples and the amounts of K that were extracted from the heated and rewet mica samples in 24 hours. Even the shortest 110°C treatment reduced the weight of the mica, but progressively more weight was lost as the heating period and temperature were increased. The rate of K release

Table 1. K extracted from 10-20 μm muscovite samples that were preheated, rewet by different treatments and then placed in NaCl-NaTPB solutions for 24 hours

<u>Preheat treatment</u>		Weight loss (%)	<u>Rewetting treatment</u>		
°C	Hrs		None	H ₂ O ^a	Steam
--K extracted (meq/100 g)--					
None		-	21.2	-	-
110	4	0.22	15.6	-	-
	8	0.26	15.3	-	-
	24	0.34	14.8	14.5	14.5 ^b
	48	0.32	14.2	-	-
200	24	0.56	12.1	11.9	12.1 ^b
300	24	0.66	10.3	9.9	9.9 ^b
350	24	0.65	10.0	-	9.8 ^c

^a H_2O at 25°C for 24 hours.

^bSteam in autoclave at 120°C , 15 psi for 1 hour.

^cSaturated H_2O vapor in pressure bomb at 110°C for 24 hours.

in the heated mica samples was also reduced by these thermal treatments. Since the weight loss in these samples had to be due to a loss of water by dehydration, the role of this hydration water in the release of interlayer K had to be considered further. To do so, heated samples were rewetted and tested for a reversal of the changes in K release rate. Simply placing the heated samples in water for 24 hours before they were mixed with NaCl-NaTPB did not produce this increase in release rate. In case this procedure did not fully rehydrate the mica, two other rehydration methods were used. Some of the heated muscovite samples were exposed to steam in an autoclave at 120°C and 15 psi pressure for 1 hour. Other samples were placed in a pressure bomb with enough water to saturate the air and produce a high pressure at 110°C for 24 hours. Neither of these rewetting procedures altered the K release rate. Thus, the reductions in K release rates that occurred when 10-20 μm muscovite samples were heated at temperatures up to 350°C do not appear to involve the hydration water and may even be irreversible.

The curves in Fig. 1 show that the extraction periods required for a maximum degree of K release by the heated mica samples varied from 4 days to 24 weeks. These differences in extraction periods reflect a variation in the net K release rates among the samples. The curves also show that a variation in K release rate existed in each sample. Thus,

information about these release rates appears to be an essential component in our understanding of the mechanisms of K release and the effects of thermal treatments. Unfortunately, the curves in Fig. 1 do not describe these rates of release very well because the extraction periods are plotted on a log scale to include the data for all the samples. On the other hand, a clear comparison of the various K release rates was obtained by calculating the average rate of release for each successive 20 meq of extractable K in the mineral samples; that is, each increment of 20 meq K/100 g mica was divided by the hours required for its extraction to obtain an average rate of meq K/100 g/hr. These values were calculated for the heated samples of 10-20 μm Keystone mica that are described in Fig. 1 and samples of the same mica that were heated at 600°C for different periods by Kozak (1976). The results are presented in three graphs to emphasize specific comparisons and to make use of different scales.

The average rates of K release for the successive 20 meq increments of K extracted from the unheated and 350°C, 24-hour heated samples are presented in Fig. 6. It is obvious that the first increment of K in the unheated mica was released at the fastest rate and that each succeeding increment was released at progressively slower rates. This is precisely the way the release rates for different portions of the K

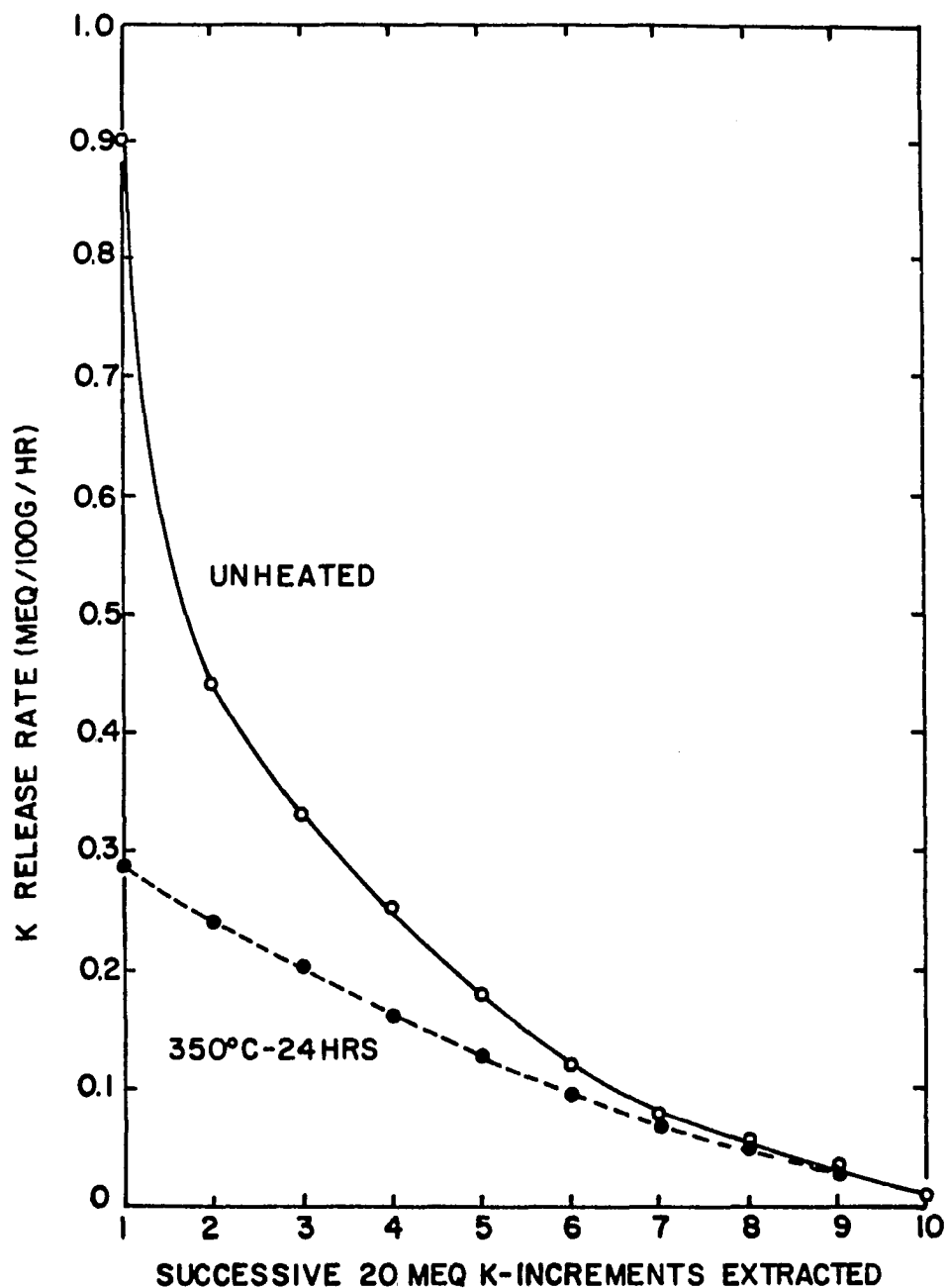


Fig. 6. Average K release rate of successive 20 meq increments of K that were extracted from 10-20 μ m muscovite samples that were heated at 350°C for 24 hours or not heated

in mica samples should vary because the release of K from coarse mica particles occurs by edge weathering and is governed by the diffusion of K from a receding weathering front to the periphery of the particle (Reed and Scott, 1962). Since the first 20 meq increment of K was close to the periphery, it had a short distance to go and was released quickly; whereas, the subsequent increments of K took a longer time to diffuse from deeper locations in the particle.

The 350°C-heated mica exhibited a similar decrease in K release rate as the origin of the extracted K shifted toward the center of the mica particles. It is evident, however, that this heat treatment reduced the release rates of all the K increments, but not to the same degree. The relative effect of the 350°C treatment on the succeeding increments of K actually decreased from a maximum at the edge to a minimum at the center of the particles. Such results might be expected if the thermal alterations in the mica were still in progress at 24 hours and had reached progressively lower stages of development toward the center of the particles. The possibility is ruled out, however, by the 350°C curve in Fig. 3, which shows the amount of K extracted in 24 hours did not vary when the heating period was increased from 10 minutes to 3 weeks. A more likely explanation for the 350°C data in Fig. 6 is that a decrease in the interlayer spacing

occurred throughout the heated mica sample. This decrease in spacing would bury the K ions deeper in the holes of the basal oxygen planes and make them more difficult to replace. With this additional restraint on the release of K, the impact of different diffusion distances on the release rates would be less and the 350°C curve in Fig. 6 should be flatter than the unheated mica curve. This concept will be developed more fully when additional data for <2 μm muscovite samples are considered.

The relative effects of different heating periods at 600, 800 and 900°C on the average release rates of successive 20 meq increments of extractable K in muscovite samples are described in Fig. 7 and 8. These results are discussed together because they all involve the effects of dehydroxylation in the mica and exhibit similar trends of an increase in rate followed by a decrease in rate as the heat treatment becomes more intensive. The unheated mica curve has been included in both figures to show the starting level for each thermally altered rate.

At a temperature of 600°C, an increase in the heating period to 2 hours produced a dramatic increase in the rate with which the initial increment of K was released. This effect would be expected because it is the outer fringe of the particles that would be dehydroxylated first. According to Kodama and Brydon (1968), mica samples that are heated in

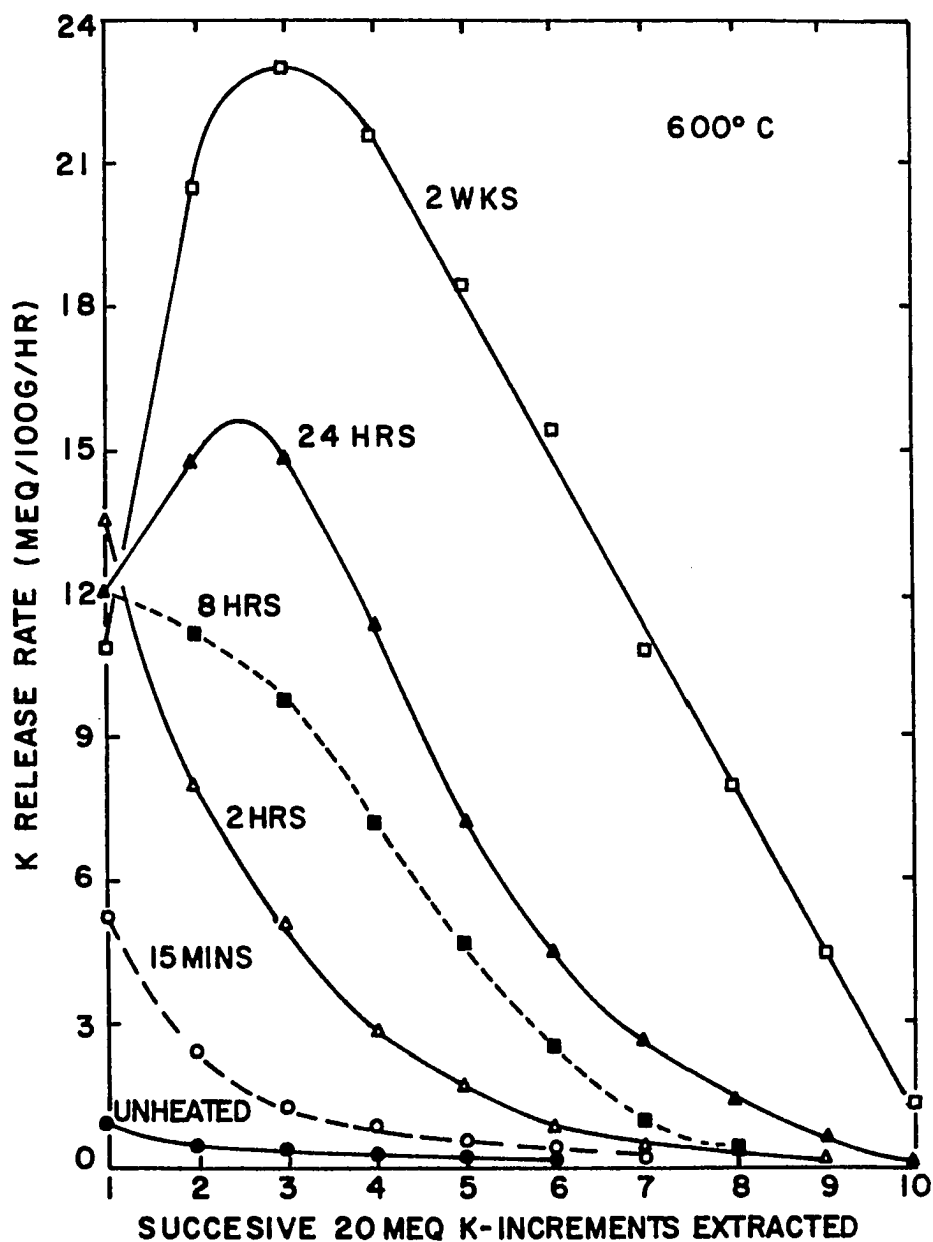


Fig. 7. Average K release rate of successive 20 meq increments of K that were extracted from 10-20 μ m muscovite samples that were heated at 600°C for different periods

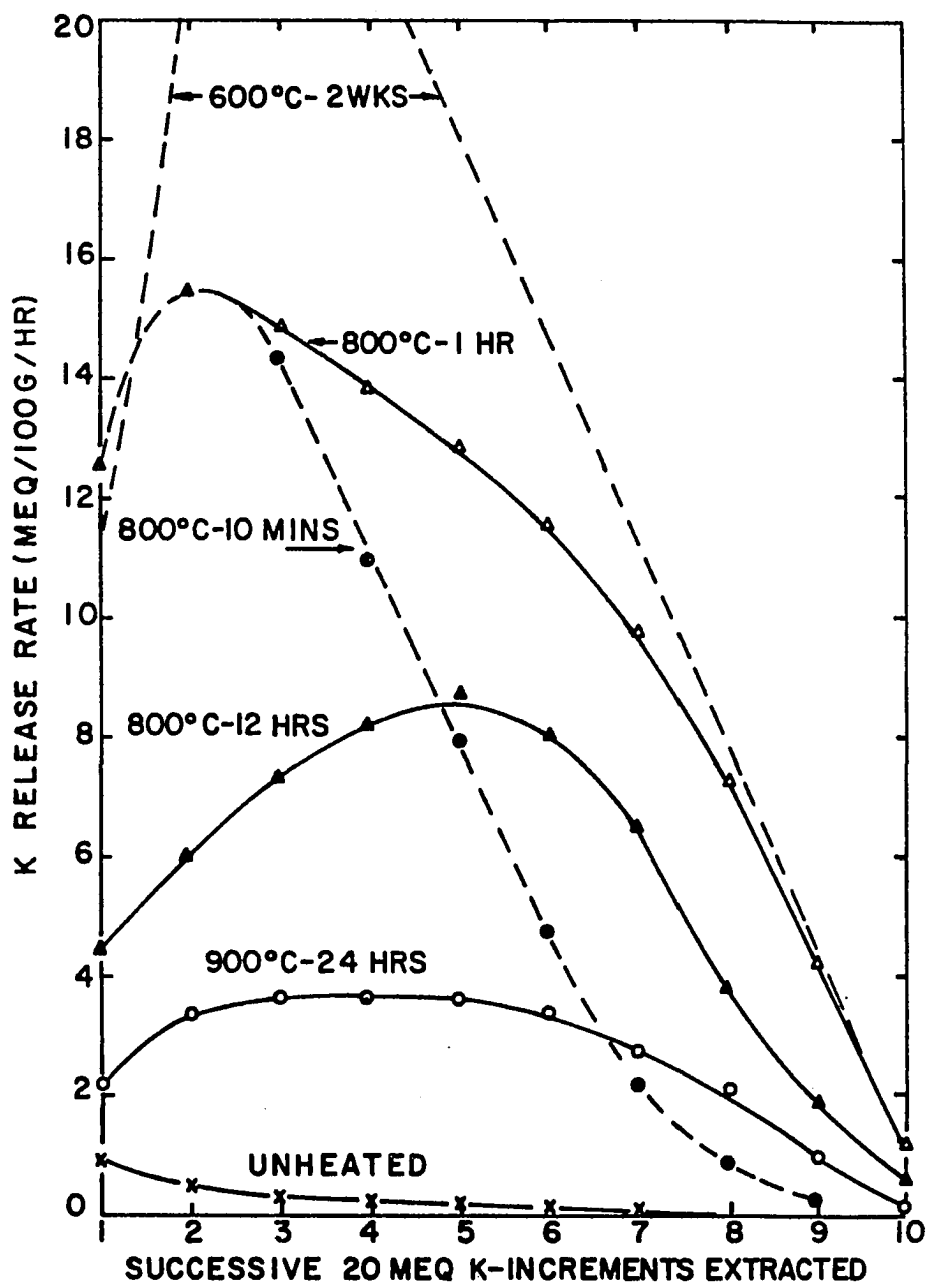


Fig. 8. Average K release rate of successive 20 meq increments of K that were extracted from 10-20 μ m muscovite samples that were heated at 800°C for different periods or 900°C for 24 hours

a vacuum oven are dehydroxylated by a homogeneous mechanism; that is, structural water is lost from an ever widening band around the rim of the mica particles. Thus, it is surprising that segments of K closer to the center of the particles and beyond the expected zone of dehydroxylation were released more rapidly after the short, 600°C treatments. These results must mean that dehydroxylation was not confined to a band at the edge of the particles. The dehydroxylation may have still involved a homogeneous mechanism, but, in this investigation, the mica samples were heated at 600°C in an unvented muffle, which allowed the released water vapor to build up around the samples. With this procedure, the system approached an equilibrium situation and the dehydroxylation progressed to a greater depth in the particles but to a lesser degree throughout the particles. Depending upon the degree of dehydroxylation, the K at various depths in the particles was rendered more exchangeable and its rate of release was increased to the extent shown in Fig. 7.

When the heating periods were increased from 15 minutes to 2 weeks at 600°C and from 10 minutes to 1 hour at 800°C, segments of the interlayer K deep in the mica particles were released at progressively higher rates. Longer heating periods at 800°C and higher temperatures (900°C) reversed this trend for the deeper K segments and actually reduced the release rates of K at all locations in the mica particles.

What happens to the first two increments of K in samples that were heated at 600°C for periods of 8 hours to 2 weeks and at 800°C for 10 minutes and 1 hour is not clear. Using the first increment of K as an example, the rate of K release increased with the heating time at 600°C, but it reached a level in 2 hours that did not change with longer heating periods or with 800°C treatments up to an hour. Based on the behavior of the deeper K segments, there is some possibility that the release rates of the edge K reflect the net effect of an increase and a subsequent decrease in the exchangeability of the K during the heat treatments. This explanation, however, would not account for the second K increment having a higher release rate in the 600°C, 2-week sample than in the 600°C, 24-hour sample. More likely, the increase in rates stemmed from a dehydroxylation of the edges, the increase was countered by a secondary alteration of the mica edges that inhibited the release of K, the observed rate remained relatively constant while the dehydroxylation and secondary process competed and finally a decrease in rate from the secondary alteration occurred when the dehydroxylation ceased. It will be shown later, in a discussion of the <2 μm heated muscovite data, that the secondary alteration of mica at high temperatures is an extension of the changes imposed by 350°C heat treatments. As stated in reference to Fig. 6, this reduction in K release rate probably

stems from a reduction in the interlayer space.

B. Muscovite Size-fractions

In the preceding experiments, the effects of thermal treatments on the exchangeability of interlayer K in micas were determined with a coarsely ground sample of 10-20 μm Keystone muscovite because the results obtained in earlier studies with <50 μm muscovite (Kozak, 1976) raised some questions about the role of very fine particles in the sample. Now, with the 10-20 μm muscovite data as a base, several other samples of Keystone muscovite with well-defined ranges of particle size were subjected to thermal treatments to determine how the changes in K exchangeability are affected by the size of the mica particles. Samples of <2 , 0.2-2, 2-5, 5-10 and 10-20 μm muscovite were selected for this comparative study.

Unheated portions of the various size-fractions were first extracted with NaCl-NaTPB solutions to establish their K release behavior. The results are presented in Fig. 9 and typify the effects of particle size on interlayer K exchange reported by Scott (1968); that is, the initial release of K increased, the maximum degree of K release decreased and the rate of K release increased as the particle size decreased. These effects of particle size have been partially explained in terms of the processes by which inter-

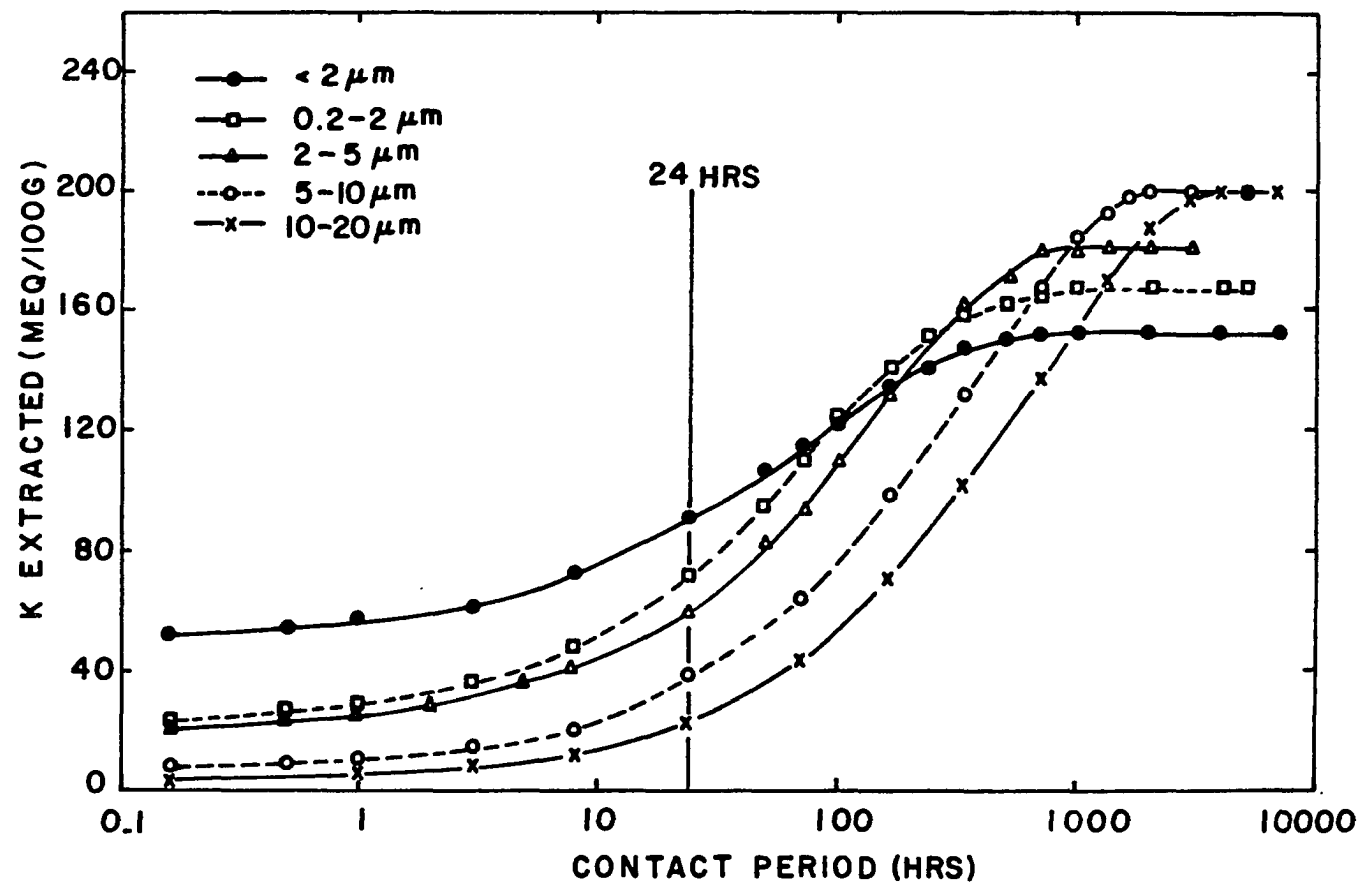


Fig. 9. K extracted from various size-fractions of ground muscovite that were placed in NaCl-NaTPB solutions for different periods.

layer K is replaced by Na. The initial release of K occurs by layer weathering, which is evidently enhanced by a decrease in particle size. The rest of the K is released by edge weathering and at a rate that is enhanced by the shorter diffusion distances and longer weathering front in smaller particles. Why the mica samples do not release all their K and release less K when the particles are smaller is still an open question (Norrish, 1972). This incomplete exchange of K in small particles (the so-called small particle effect) seems to be related to the occurrence of layer weathering and has been attributed by some people to interactions between the K and structural OH groups. Thus, there are several features about the K release behavior of small mica particles that need to be evaluated in terms of their alteration by thermal treatments. Much of this information was obtained from a detailed comparison of the responses of $<2\text{ }\mu\text{m}$ and $10\text{-}20\text{ }\mu\text{m}$ samples which will be described later. The use of all the size-fractions was confined to the effects of particle size on the rates of K release in heated samples. For this purpose, the amounts of K extracted in a 24-hour period were used as an index of the rate of K release. The location of this 24-hour period on the various K release curves is shown in Fig. 9.

The effects of thermal treatments on the rate of K release in the various mica size-fractions are described in

Fig. 10. These data were obtained by heating the mica samples at different temperatures for 24 hours and then placing them in NaCl-NaTPB solutions for 24 hours to extract K. In general, the various size-fractions responded to the thermal treatments in a similar manner, in that the release rate first decreased, then increased and finally decreased again when all the samples were subjected to progressively higher temperatures. Differences in the degree of these changes and the temperature required, however, were encountered with the various size-fractions. As the particle size decreased, the initial reduction in release rate became more pronounced, the increase occurred at a lower temperature, the maximum rates achieved at temperatures around 700°C were lower and the final reductions in rate occurred at higher temperatures and to a lesser degree. Explanations for many of these effects of particle size will be discussed later with the more extensive data for the <2 μm sample. Of interest here are the relative changes in K exchangeability that might be related to the processes of dehydration and dehydroxylation in the heated particles of different size.

The curves in Fig. 11 describe the weight loss that occurred in the heated samples and, thus, the occurrence of dehydration and dehydroxylation in the various size-fractions. It is evident that the amount of hydration water

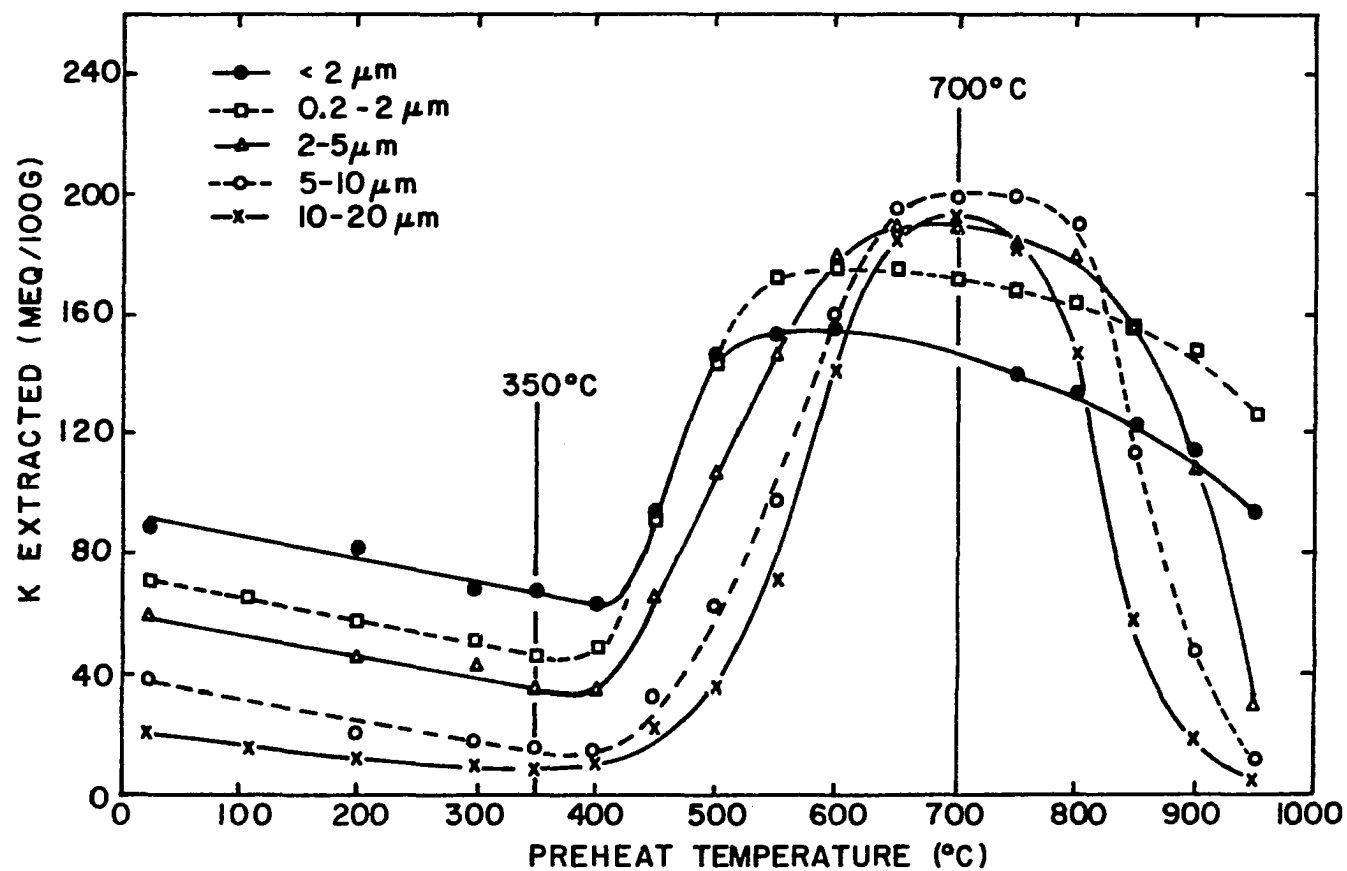


Fig. 10. K extracted from various size-fractions of ground muscovite that were heated at different temperatures for 24 hours and then placed in NaCl-NaTPB solutions for 24 hours

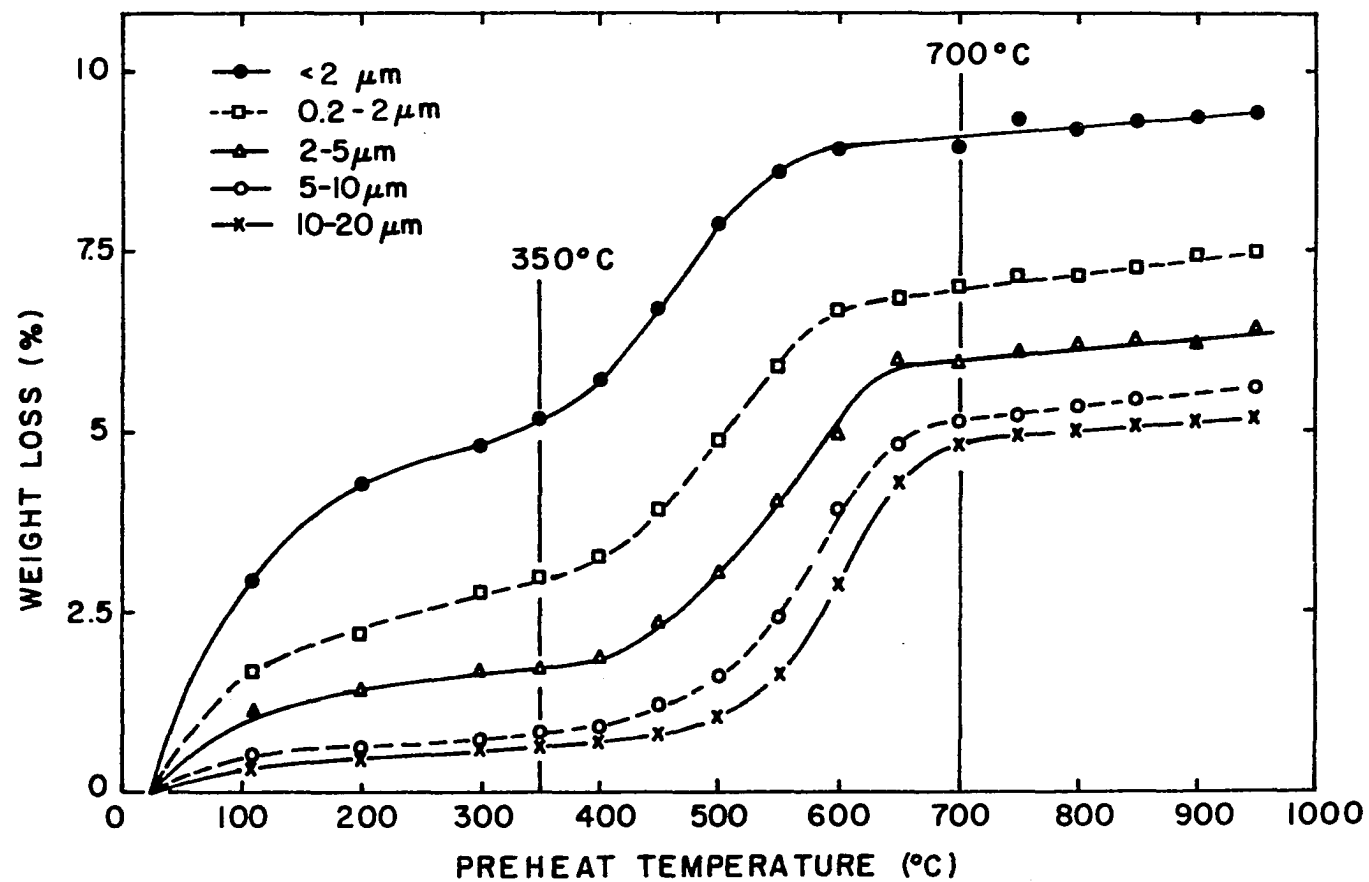


Fig. 11. Weight loss by various size-fractions of ground muscovite that were heated at different temperatures for 24 hours

increased appreciably as the particle size decreased, but the removal of this water produced no proportionate changes in the K release rate. This observation supports an earlier conclusion from Table 1 that hydration water has little effect on the release of interlayer K by micas. On the other hand, the various size-fractions lost about the same amount of water by dehydroxylation. Based on the heating temperatures involved, the dehydroxylation and increase in K release rates appear to be related, as would be expected from the data in Fig. 5. The onset of dehydroxylation in the different samples is not well-defined but there is some indication that it occurred at lower temperatures in the smaller particles and accounted for the lower temperatures at which the increase in K release occurred. For some reason, the rate changes in the smallest particles stopped before the mica was fully dehydroxylated. This relationship is brought out more clearly in Fig. 12, where curves for the weight loss and K release rates in the 0.2-2 μm size-fraction are presented. Temperatures above 550°C produced no increase in the K release rate but did cause more dehydroxylation. This behavior of the small mica particles will be discussed with similar results for the <2 μm mica, but it should be noted here that it was not due to the presence of very fine <0.2 μm particles.

Experiments were carried out with samples of <2 μm

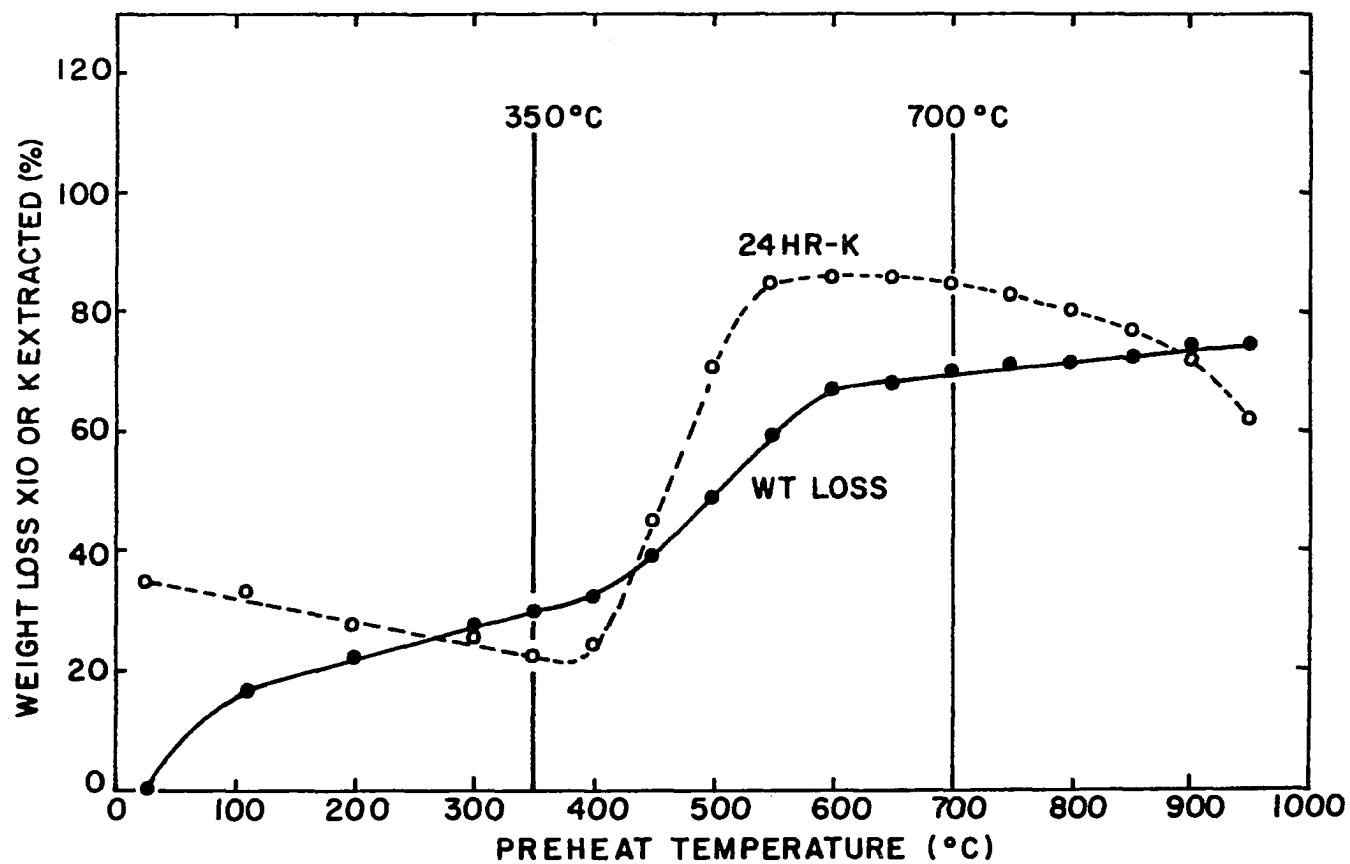


Fig. 12. Weight loss by 0.2-2 μm muscovite samples that were heated at different temperatures for 24 hours and K extracted by placing the heated samples in NaCl-NaTPB solutions for 24 hours

Keystone muscovite to obtain detailed information about the effects of thermal treatments on the exchangeability of K in small mica particles. Each of these experiments was designed to provide results that could be compared with those obtained with the 10-20 μm mica samples.

The curves in Fig. 13 describe the K release behavior of <2 μm muscovite samples that were heated at different temperatures for 24 hours. The K release curve for the unheated <2 μm samples is obviously quite different from that obtained with 10-20 μm mica. These differences have been described and accounted for in the discussion of Fig. 9. Particularly significant is the fact that fine mica particles release large amounts of K by layer weathering as soon as they are placed in the NaCl-NaTPB solutions. When the fine particles were heated, this release of K by layer weathering decreased. The subsequent release of K by edge weathering in the <2 μm and 10-20 μm samples responded similarly to thermal treatments in that the rate of release was first reduced by 350°C treatment, increased by higher temperatures and finally reduced again by even higher temperatures. On the other hand, the effects of thermal treatments on the maximum degree of K release were more complex in the smaller particles. Overall, these results made it clear that the effects of thermal treatments on the exchangeability of K in small mica particles were distinctive enough to warrant further study.

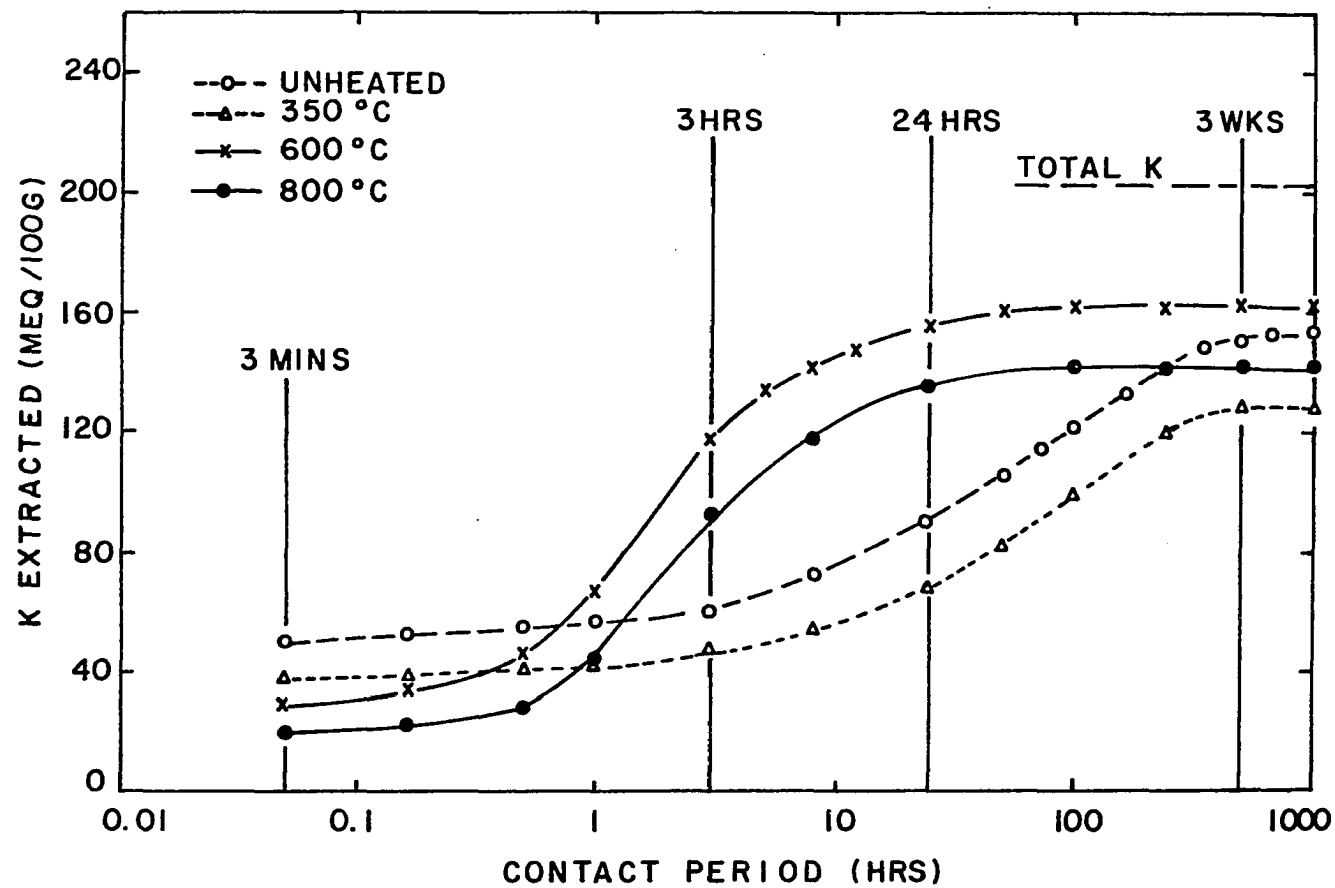


Fig. 13. K extracted from $<2 \mu\text{m}$ muscovite samples that were heated at different temperatures for 24 hours, then placed in NaCl-NaTPB solutions for different periods

Samples of $<2\text{ }\mu\text{m}$ muscovite were heated at different temperatures for 24 hours and then placed in NaCl-NaTPB solutions for selected extraction periods. Extraction periods of 3 minutes and 3 weeks were used for information about the effects of the thermal treatments on the initial release of K by layer weathering and the maximum degree of K release, respectively. The rates of K release at different stages of the process were determined with extraction periods of 3 hours and 24 hours. The locations of these extraction periods on the K release curves are shown in Fig. 13; the amounts of K extracted are reported in Fig. 14.

The 3-minute K curve describes the changes in layer weathering that occurred when the $<2\text{ }\mu\text{m}$ samples were preheated at progressively higher temperatures. Whereas the $10\text{-}20\text{ }\mu\text{m}$ muscovite particles released no more than 2% of their K by layer weathering, the unheated $<2\text{ }\mu\text{m}$ sample released 24% of its K by this mechanism. When the smaller particles were heated, the amount of layer weathering decreased as the temperature was increased. These results would suggest that the heat treatments enhanced the bonds with which interlayer K holds the mica layers together. According to Takeda and Morosin (1975), heating can reduce the amount of Si tetrahedra rotation in micas. This untwisting of the tetrahedra would enlarge the hexagonal hole, allow K to sink deeper into the basal oxygen planes, reduce

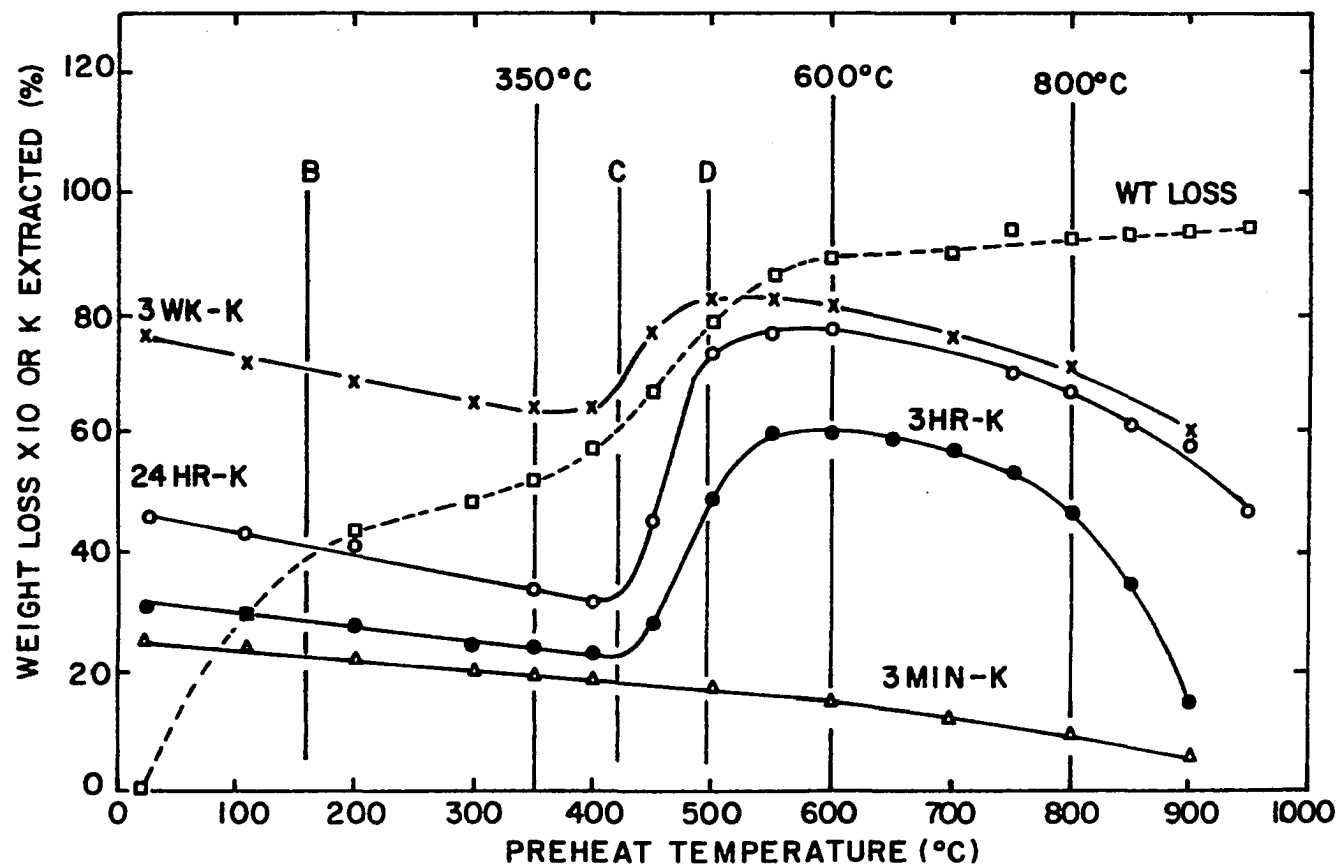


Fig. 14. Weight loss by $<2 \mu\text{m}$ muscovite samples that were heated at different temperatures for 24 hours and K extracted by placing the heated samples in NaCl-NaTPB solutions for 3 minutes, 3 hours, 24 hours and 3 weeks

the interlayer spacing and make layer weathering less likely. It will be noted later, however, that X-ray diffraction measurements did not verify the occurrence of these structural alterations.

In a discussion about the K release curves in Fig. 9, it was noted that the maximum degree of K release decreased as the size of the mica particles decreased. Due to this small particle effect, the $<2\ \mu\text{m}$ sample released only 76% of its K, whereas the 10-20 μm sample released 93%. Unfortunately, as shown by the 3-week curve in Fig. 14, this small particle effect was not eliminated by heating. Instead, samples that were heated at temperatures up to 350°C released even less K. An increase in the heating temperature over the range causing dehydroxylation reversed this trend and raised the maximum degree of K release to 82%. Higher temperatures, however, caused another downward trend in K exchangeability. This variation in the maximum K release by the $<2\ \mu\text{m}$ mica was much greater than that observed with the 10-20 μm samples and seems to be linked with the effects of thermal treatments on layer weathering (3-minute curve). If the thermal treatments contracted the mica enough to reduce layer weathering, as suggested earlier, it is equally possible that some of the interlayer K could be rendered non-exchangeable. This relationship between layer weathering and maximum release seems to contradict earlier suggestions

that increases in layer weathering in unheated samples of small mica particles cause a decrease in maximum K release (Scott, 1968). However, the two concepts are compatible in terms of the interlayer K status, in that some of the K in mica can be rendered less exchangeable by either an expansion of adjacent layers or a contraction of interlayers.

The effects of thermal treatments on the rates of K release by $<2\ \mu\text{m}$ mica are described by the 24-hour and 3-hour curves in Fig. 14. The general features of the 24-hour results have been described earlier with the results for several size-fractions (Fig. 10). The curve in Fig. 14 provides the additional information that the increase in release rate (CD) coincided with the occurrence of dehydroxylation but did not continue to the point of complete dehydroxylation. Moreover, it is evident from Fig. 14 that the increase in release rate from C to D did not continue to increase with higher temperatures (as was observed with coarse size-fractions) because the 24-hour period extracted nearly all the exchangeable K. The similar behavior of the $0.2\text{--}2\ \mu\text{m}$ sample (Fig. 12) probably occurred for the same reason. When a 3-hour extraction period was used with the $<2\ \mu\text{m}$ sample, an increase in heating temperature from 450 to 900°C produced a curve that was shaped more like those of the coarse micas. Even so, it would appear that the high temperatures (800 and 900°C) did not slow down the release

rate as much in the small particles as they did in the coarse particles. If this reduction in rate were due to a contraction of the mica, as was suggested for the 10-20 μm sample, the effect of this contraction on the exchangeability of interlayer K must be less in small particles.

The maximum levels of K release by mica samples represent a combination of the K released by layer and edge weathering. Thus, it was an easy matter to determine the changes in edge weathering that occurred in the heated $<2 \mu\text{m}$ samples. The amounts of K released by edge and layer weathering are shown in Fig. 15. A curve showing the weight lost by the heated mica has been included to relate the occurrence of dehydration and dehydroxylation with the K release processes. Parallel straight lines were drawn through the layer K data and through the initial and final segments of the edge K results to compare the effects of thermal treatments on the two modes of K release.

It is evident from the three parallel lines that the heat treatments altered the layer weathering and segments of the edge weathering in a very comparable manner. Except for an increase in edge release in the samples heated at 400 to 500°C, an increase in temperature produced a progressive reduction in the K released by both mechanisms. A decrease in the interlayer spacing of the heated mica could very well account for all these reductions in K release.

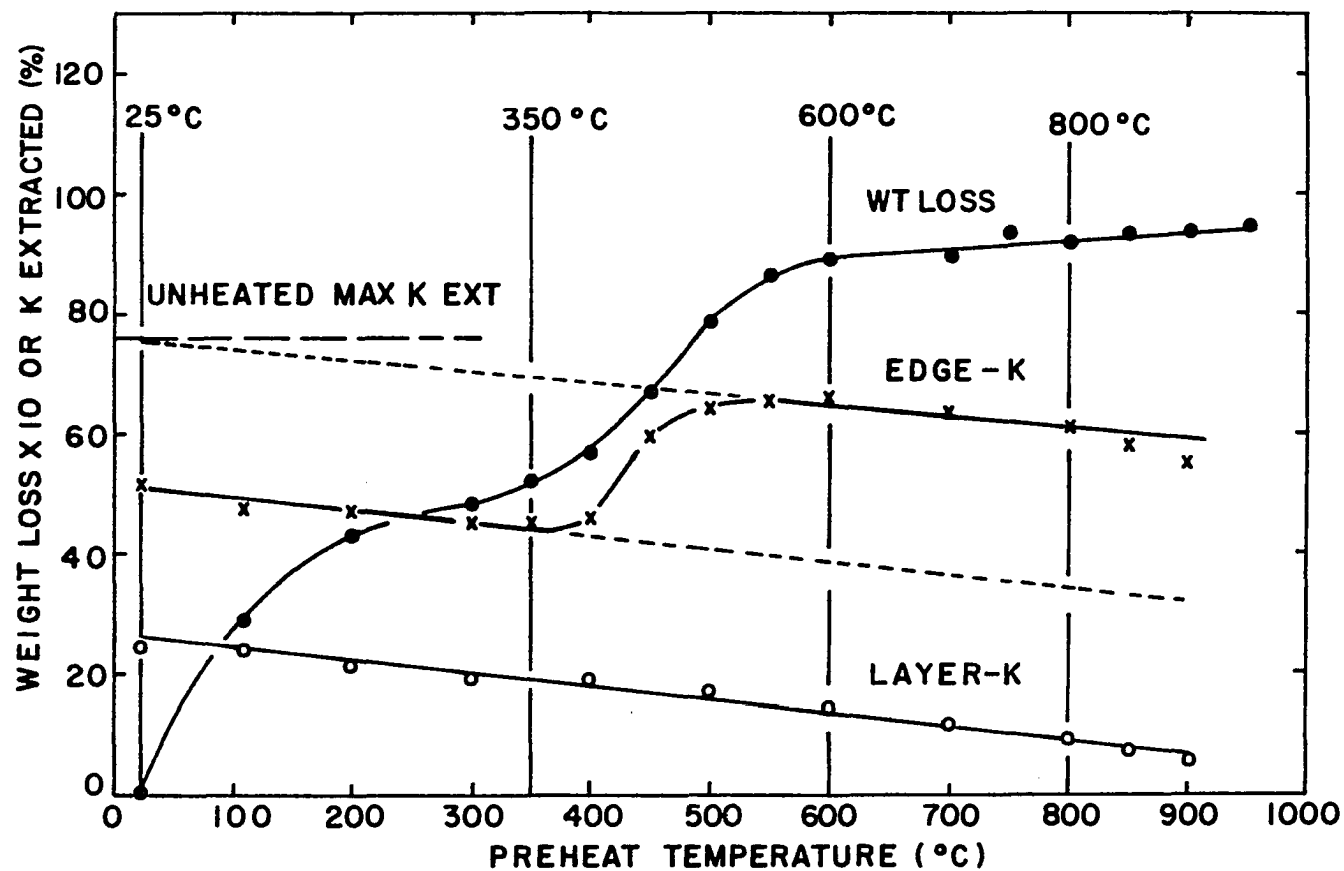


Figure 15. Weight loss by $<2 \mu\text{m}$ muscovite samples that were heated at different temperatures for 24 hours and K extracted by placing the heated samples in NaCl-NaTPB solutions to obtain layer and edge release

The only other thermal alteration that seems to be involved is the loss of structural water by dehydroxylation in the samples heated at 400 and 500°C. The effects of dehydroxylation are obviously great enough to offset the thermally induced reductions in K release.

If the straight line through the high temperature position of the edge K curve is extrapolated to 25°C (as shown by the dotted line in Fig. 15) to eliminate the effects of heating, an edge release of 76% of the K would be predicted for unheated samples. A combination of the edge release with the 24% release by edge weathering would suggest that all the interlayer K in unheated <2 μm particles could be exchangeable if the effects of dehydroxylation could be achieved without the other thermal alterations. At present, progress toward this goal is hampered by inadequate information on the mechanisms by which the dehydroxylation and thermal treatments produce the changes in K exchangeability. Some means of increasing the interlayer spacing (as dehydroxylation does) without heating the mica (which appears to contract the mica) seems to be needed. In any event, the precise interlayer spacing appears to be emerging as a dominant factor governing interlayer K exchangeability.

It was observed with 10-20 μm mica samples that the heating period as well as the heating temperature had a pronounced effect on the exchangeability of interlayer K. Thus,

similar experiments were carried out with $<2\text{ }\mu\text{m}$ muscovite by using selected temperatures and a range of heating periods. With this fine-grained mica, K extraction periods of 3 hours and 3 weeks were used to determine the effects of these thermal treatments on the release rate and maximum release. Weight loss determinations were also carried out with each of the heated samples. The K release and weight loss results are presented in Fig. 16 and 17, respectively.

Compared with the $10\text{--}20\text{ }\mu\text{m}$ response to heating periods (Fig. 3 and 4), the $<2\text{ }\mu\text{m}$ samples exhibited relatively little change in K exchangeability. Only the 600°C samples lost appreciably more water as the heating period was increased from 10 minutes and gave a corresponding increase in rate of K release. At 800°C , the changes in weight probably occurred in a period of less than 10 minutes and only small decreases in K exchangeability were induced by longer periods. The 350°C temperature was too low to remove more than the hydration water but it did cause some decrease in the exchangeability of K in the smaller particles. All these results are pretty much in line with the expectation that smaller particles would require shorter heating periods for similar thermal alterations. It should be added, however, that these $<2\text{ }\mu\text{m}$ mica results provide clear evidence that the heating temperature is more important than the heating period when the thermal treatment is intensive enough to

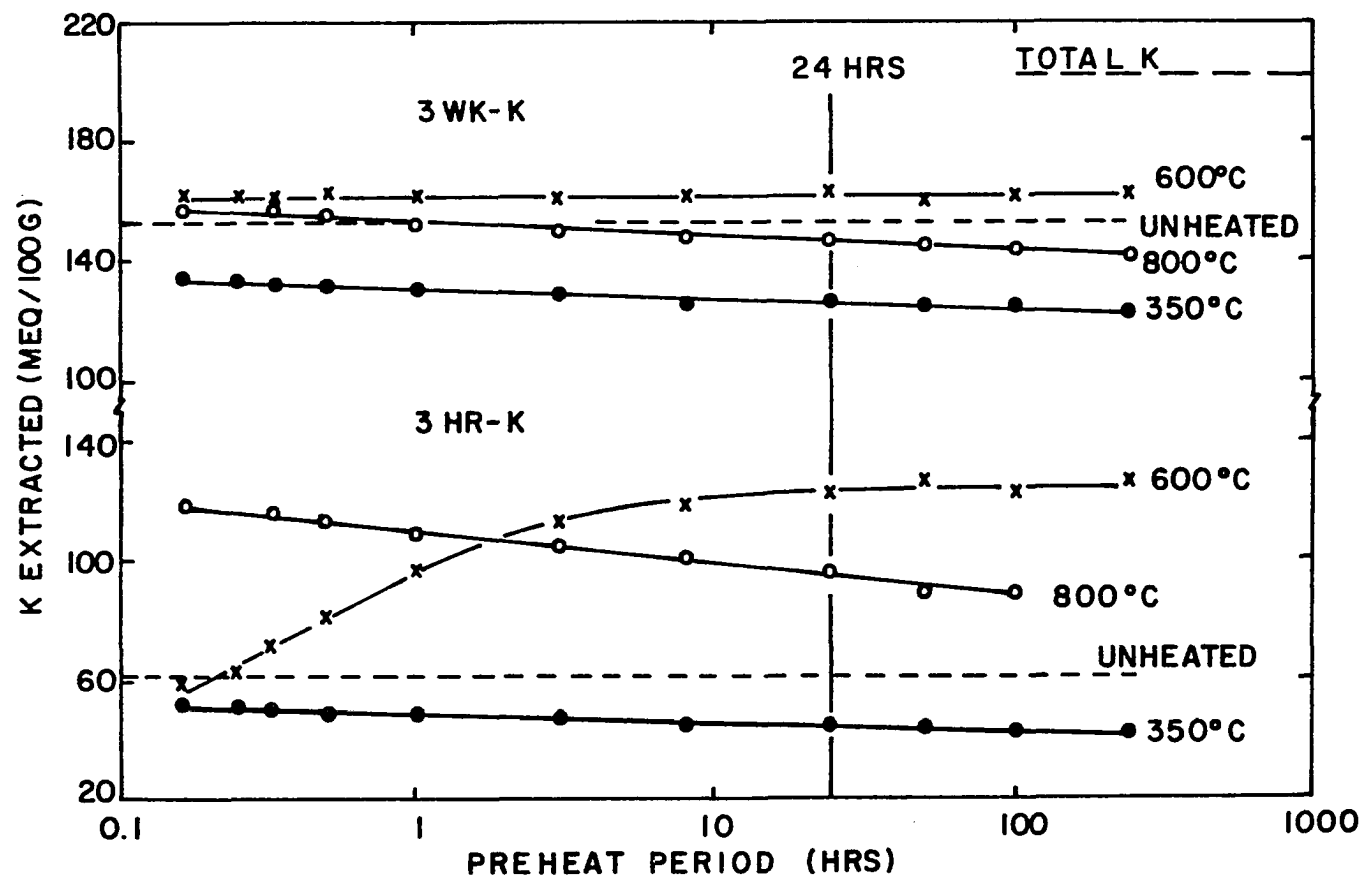


Fig. 16. K extracted from $<2 \mu\text{m}$ muscovite samples that were heated at different temperatures for different periods, then placed in NaCl-NaTPB solutions for 3 hours and 3 weeks

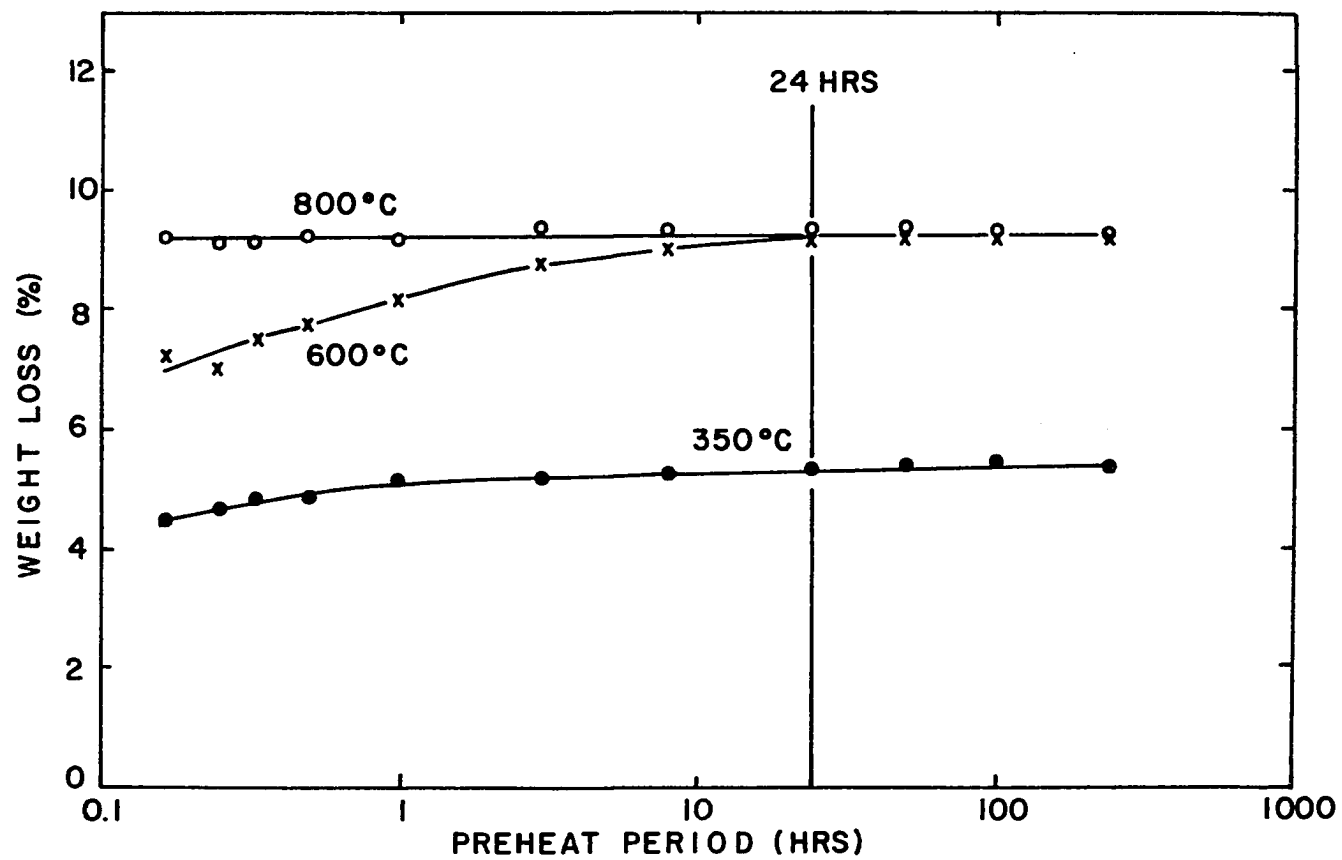


Fig. 17. Weight loss by <2 μm muscovite samples that were heated at 350, 600 and 800°C for different periods

decrease the exchangeability of K in dehydroxylated mica. Samples heated as long as 3 weeks at 600°C exhibited no decrease in maximum degree or rate of K release. Short heating periods at 800°C reduced both.

A comparison of the 24-hour K and weight loss curves in Fig. 14 provides some indication that the K release rate is somehow related to the loss of water. By using many more heating periods at each temperature, the relationship between the K release rate (24-hour extractable K) and the weight loss in <2 μ m mica samples was developed more fully. The results are shown in Fig. 18.

Little change in K release rate occurred as the weight loss increased to point B (3.6%). At this stage of the thermal treatments, the weight loss involved only dehydration but not a complete loss of hydration water (Fig. 14). Thus, earlier conclusions about the irrelevance of hydration water to K exchangeability have been borne out by these <2 μ m mica results. A further loss of weight from B to C, however, caused a decrease in release rate even though this weight loss stemmed from a combination of dehydration and dehydroxylation which should have caused either no change or an increase in release rate. Despite the good relationship between the release rate and weight loss between B and C in Fig. 18, it seems more likely that a second thermal effect, such as the contraction of mica suggested

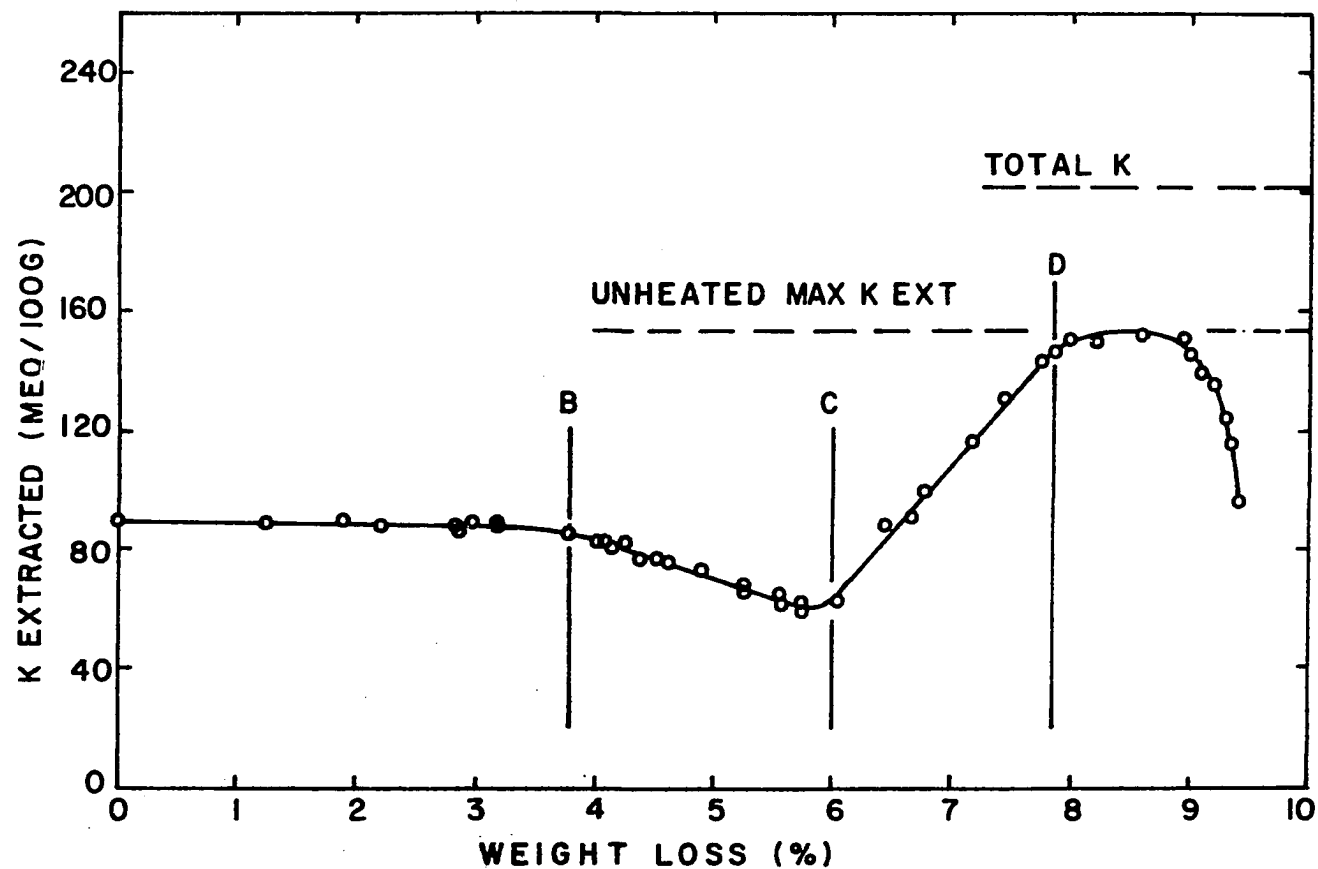


Fig. 18. Relationship between the K released by heated $<2 \mu\text{m}$ muscovite samples in NaCl-NaTPB solutions for 24 hours and the mica weight loss during the heat treatments

for the 10-20 μm sample, reduced the rate of K release in the $<2\ \mu\text{m}$ mica. Unlike the coarse-grained mica, the $<2\ \mu\text{m}$ mica did not exhibit a sharp increase in release rate (b to c in Fig. 5) before a less rapid increase due to dehydroxylation occurred. Instead, the release rate increased from C to D in a uniform manner as dehydroxylation occurred. This difference in behavior must have been due to the particle size involved. If so, the changes in release rate probably stemmed from an increase in interlayer spacing (due to the expulsion of H_2O) rather than a reduction in the OH-K interactions in the mineral.

Reductions in the rate of K release occurred when the heated $<2\ \mu\text{m}$ samples lost more than 9% of their weight. The changes in release rate, however, were not as dramatic as in the coarse mica and do not appear to be due to the loss of water.

Since dehydroxylation occurred in the muscovite samples that exhibited an increase in K exchangeability due to heating, attention was given to ways of controlling the dehydroxylation and, thereby, of testing the relationship between these thermal effects. When dehydroxylation occurs, structural OH groups in the mica combine to form water which is then expelled. An increase in the water vapor around the heated mica particles should inhibit this process by counteracting the expulsion of water molecules from the mineral. Thus,

samples of $<2\text{ }\mu\text{m}$ muscovite were heated in a pressure bomb with enough water to create a high vapor pressure of water at different temperatures. These experiments were limited to a maximum temperature of 500°C to stay well within the safety limit of 600°C for the bomb. Each sample was heated for 24 hours and then placed in NaCl-NaTPB solutions for 24 hours to extract K. No weight loss determinations could be made, because some of the water vapor condensed on the mica when the bomb was cooled. The amounts of extracted K are reported in Fig. 19. The 24-hour K release results from experiments with samples heated in a regular oven (Fig. 14) are also described in Fig. 19 by a curve without data points.

When the $<2\text{ }\mu\text{m}$ mica samples were heated in the bomb at temperatures of 450 and 500°C , the increase in K release due to dehydroxylation in the regular oven did not occur. Thus, the bomb method must have inhibited the dehydroxylation process successfully and provided direct evidence that dehydroxylation is responsible for the increase in K exchangeability. At the lower temperatures, the regular oven treatment caused some reduction in the K release rate but an even greater reduction occurred in the samples from the bomb. These reductions in the bomb cannot be attributed to a loss of water by dehydration or dehydroxylation. Instead, they probably reflect the entire reduction in K release that can be imposed by a contraction of the mica, whereas the results

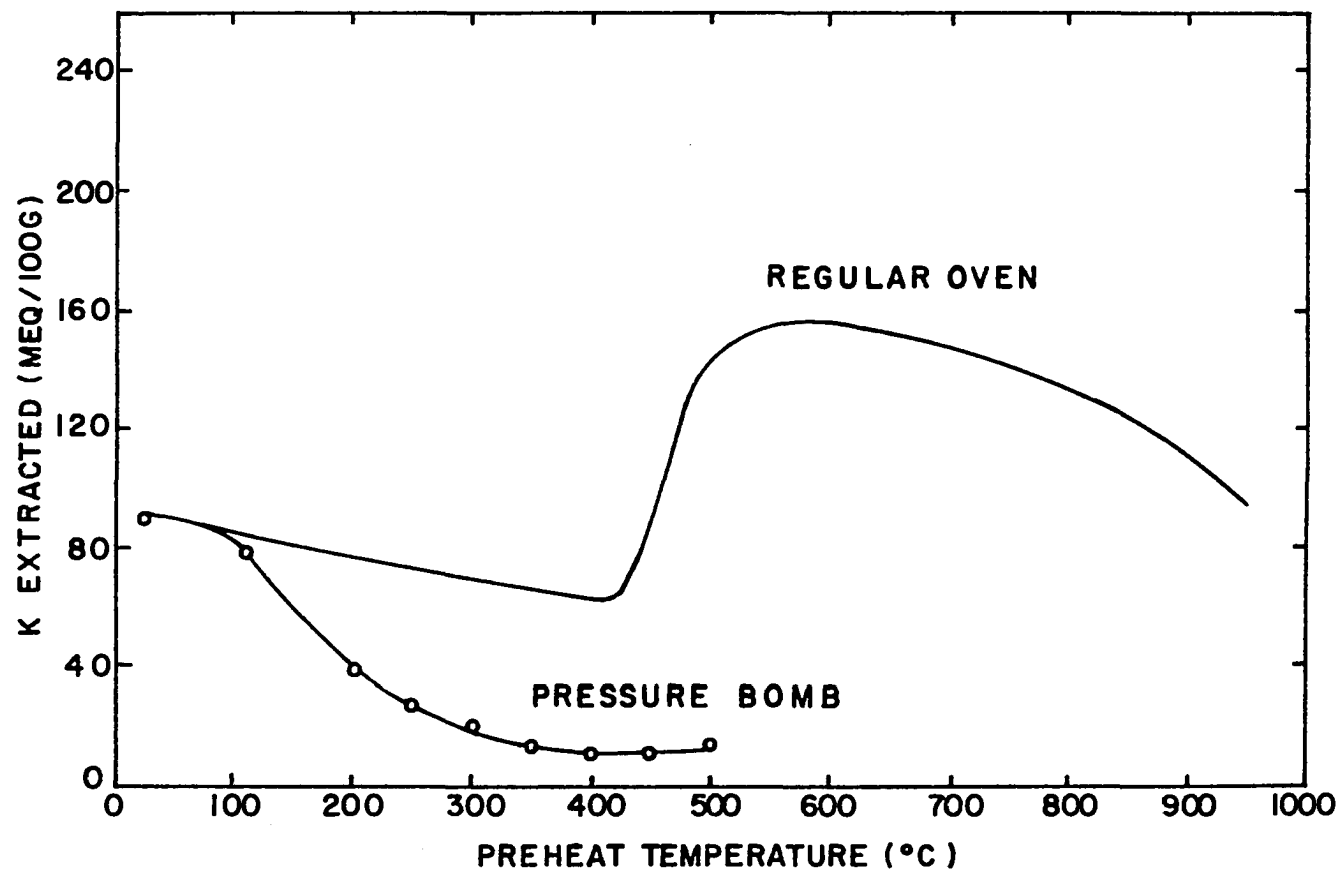


Fig. 19. K extracted from $<2 \mu\text{m}$ muscovite samples that were heated in a regular oven (air) or a pressure bomb (H_2O saturated atmosphere) at different temperatures for 24 hours and then placed in NaCl-NaTPB solutions for 24 hours

reported for the regular oven have been modified to various degrees by an opposing effect from the loss of water.

Explanations for the decrease in the exchangeability of K in heated samples of the various muscovite size-fractions have focused on the possibility that the thermal treatments caused a reduction in the interlayer spacing. This concept should be subject to confirmation by X-ray diffraction measurements of the basal spacings in heated and unheated samples of the muscovite. It was stated earlier in connection with the results in Fig. 5, that X-ray diffraction studies yielded no evidence of a decrease in basal spacing in heated samples of 10-20 μm muscovite. An even better opportunity to observe this change in basal spacing arose with the $<2 \mu\text{m}$ mica samples that were heated in a pressure bomb to avoid dehydroxylation and achieve a major reduction in K exchangeability.

Samples of $<2 \mu\text{m}$ mica were heated in the regular oven at 400°C and in the pressure bomb at 400 and 500°C . These heated samples were cooled in a desiccator, mixed with corundum and water and sedimented on ceramic slides. Sedimented specimens of the unheated $<2 \mu\text{m}$ mica were prepared in the same manner. In each case, the corundum provided three diffraction peaks which were used to normalize the diffraction patterns. The results, however, failed to provide any evidence for a decrease in the basal spacings of the heated

mica. Using Ni filtered Cu radiation, the $d(00.10)$ reflections (5th order for $2M_1$ muscovite) occurred at 2θ angles of 45.38, 45.40, 45.42 and 45.42° for the unheated, 400°C -regular oven, 400°C -bomb and 500°C -bomb samples, respectively. Thus, there was actually a small increase of about 0.002 \AA in the basal spacing of the 500°C -bomb sample. Perhaps the heat treatment caused structural rearrangements that thickened the mica layers enough to over compensate for decreases in the interlayer spacing. Only a detailed structural analysis of the original and heated mica would verify this point.

C. Illites

Since macrocrystalline muscovites exist in the form of large sheets, they have to be ground to a finely divided state before they can be used for K release studies. Whether this grinding treatment alters the micas enough to have a significant effect on their K release behavior is still being debated. The heat generated by dry grinding procedures can presumably cause mineral alterations (Mackenzie and Milne, 1953) but grinding by any process will determine the nature of the particle edges and thereby affect the onset of K release (Newman and Brown, 1969). Moreover, it is evident from the review by Norrish (1972) that the effects of grinding are not easily segregated from the effects of small

particles. Thus, for the present study of the effects of thermal treatments on interlayer K exchangeability, consideration was given to differences that might arise from the use of naturally occurring, fine-grained illites instead of the ground muscovite. The $<2\ \mu\text{m}$ Keystone muscovite data were used as a reference and comparisons were made with the results obtained with $<2\ \mu\text{m}$ size-fractions of Tumut and Grundite illites.

Tumut illite is a naturally occurring, fine-grained, dioctahedral micaceous mineral that is well-crystallized and contains essentially no expanded layers. Thus, this particular illite offered a good opportunity to compare the effects of thermal treatments on naturally occurring and ground samples of $10\ \text{\AA}$ micaceous minerals. To make this comparison, samples of the $<2\ \mu\text{m}$ size-fraction in the Tumut illite were subjected to various heat treatments and placed in NaCl-NaTPB solutions to extract K. The amount of K release that occurred in different extraction periods with unheated and heated samples of the Tumut illite is shown by the curves in Fig. 20.

The K release behavior of the $<2\ \mu\text{m}$ unheated Tumut differed from that of $<2\ \mu\text{m}$ ground muscovite. Whereas the unheated Tumut released only 4 meq K/100 g initially, the ground muscovite released nearly 50 meq/100 g. This difference in initial K release can be attributed to the relative

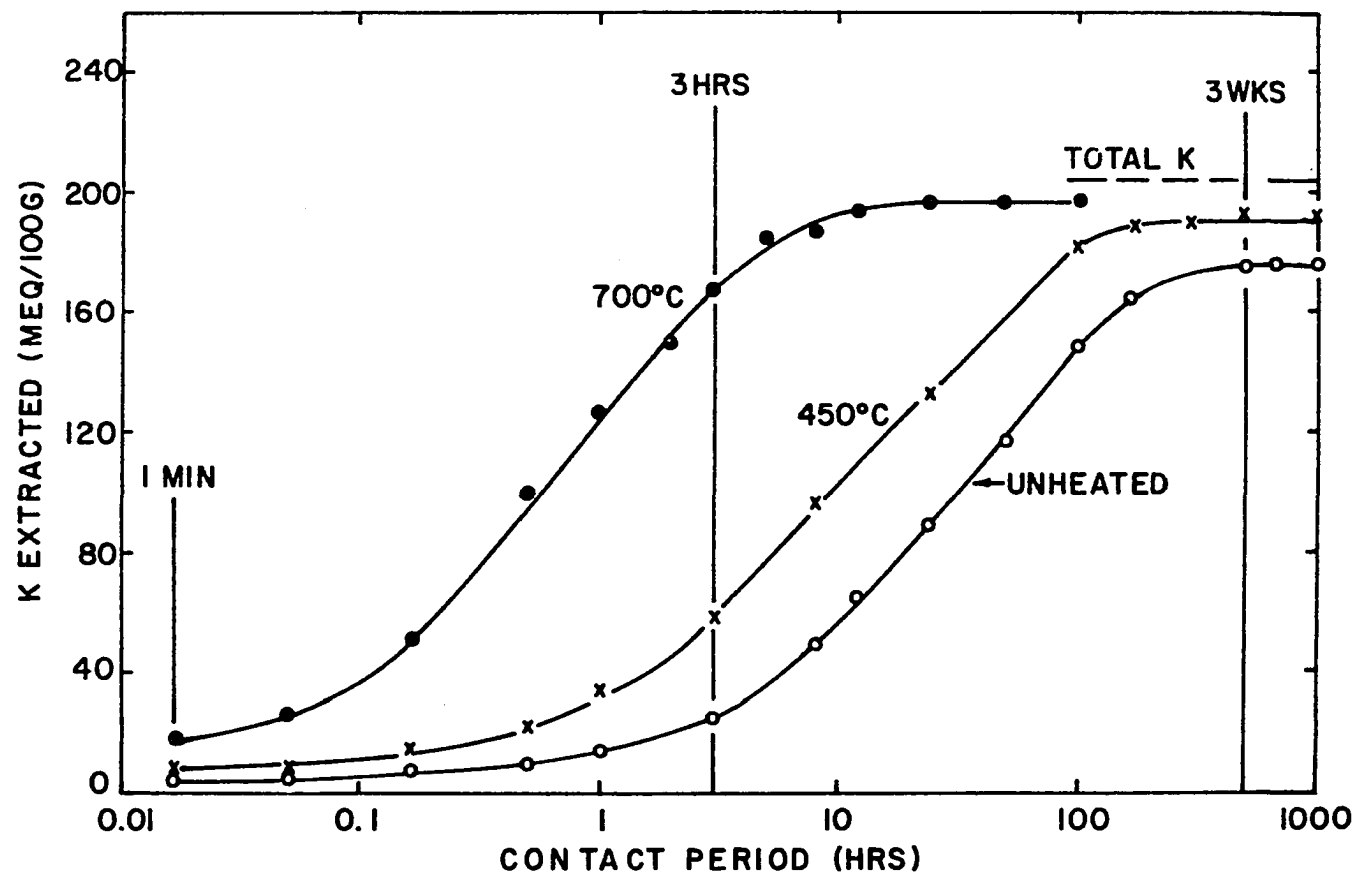


Fig. 20. K extracted from $<2 \mu\text{m}$ Tumut illite samples that were heated at different temperatures for 24 hours and then placed in NaCl-NaTPB solutions for different periods

condition of the lateral edges of the two mineral particles. When muscovite sheets are ground to obtain small particles, a complete separation of some mica layers (cleavage) no doubt occurs, but most particles are left with incipient layer separation at their newly exposed edges. As soon as these particles are placed in NaCl-NaTPB solutions, an exchange of hydrated Na for interlayer K at the lateral edge provides enough force to complete the separation of some layers. By this means, large amounts of K are extracted very quickly by the so-called "layer weathering" process (Scott, 1968). On the other hand, the Tumut particles have been exposed to natural weathering processes that should have removed most of the edge exposed K and incipient layer separation. As a result, the unheated Tumut particles exhibited little layer weathering in the NaCl-NaTPB solution and the thermal treatments did not reduce the initial release of K as they did in muscovite.

Since there was less layer weathering in the Tumut sample, it was not surprising that the maximum degree of K release in the unheated Tumut (86%) was greater than the 76% in ground muscovite. Heat treatments made even more of the K in the Tumut exchangeable and had enough effect on the maximum K release to warrant a search for ways of extracting all the K, an accomplishment not yet achieved with $<2 \mu\text{m}$ particles of any micaceous mineral.

The 450 and 700°C treatments enhanced the rate of K release by edge weathering in the Tumut samples as they did with muscovite. By doing so, they also provided evidence that the Tumut particles released K by edge weathering from the beginning of the NaCl-NaTPB treatment. More important is the fact that this edge release of K in the Tumut particles was measurable in a matter of minutes, whereas even the heated muscovite took much longer. This difference may be due to the particle size distribution in the two <2 µm samples, but it could mean that the interlayer K is not held as strongly in the Tumut particles. This point will be discussed further with the corresponding Grondite illite data.

A detailed study of the effects of the thermal treatments on the exchangeability of K in the Tumut illite was carried out with samples that were heated at temperatures of 110 to 950°C for 24 hours. Each sample was weighed before and after the heat treatment to determine its weight loss. The heated samples were placed in NaCl-NaTPB solutions for periods of 1 minute, 3 hours, and 3 weeks to determine the effects of the thermal treatments on the initial K release, the rate of K release, and the maximum degrees of K release, respectively. These extraction periods are marked in Fig. 20 to show the stages of K release involved.

A comparison of the Tumut results in Fig. 21 with those reported in Fig. 14 for <2 µm muscovite show that few simi-

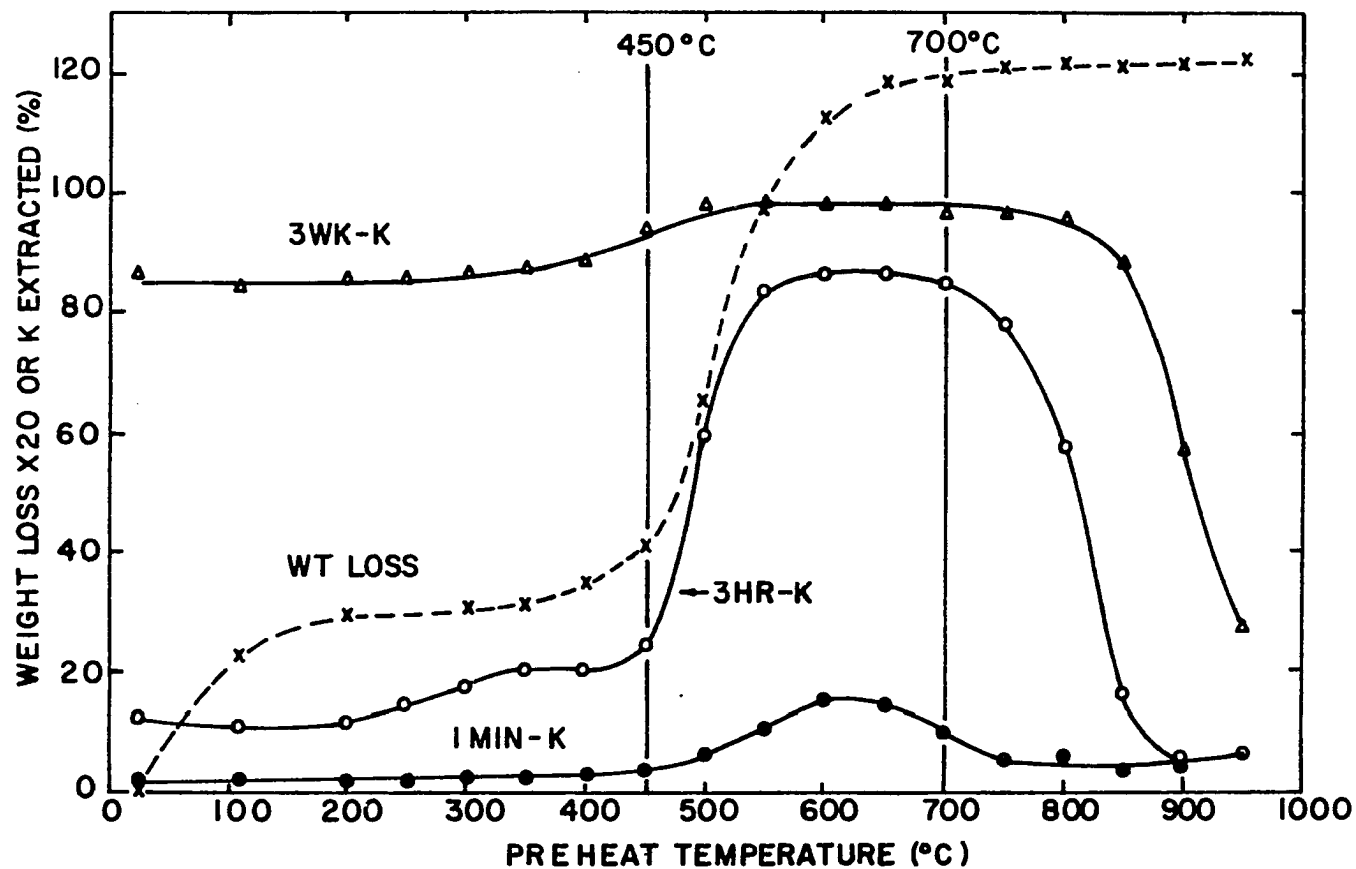


Fig. 21. Weight loss by <2 μ m Tumut illite samples that were heated at different temperatures for 24 hours and K extracted by placing the heated samples in NaCl-NaTPB solutions for 1 minute, 3 hours and 3 weeks

larities exist. In both cases, the release rate and weight loss increased together at temperatures above 400°C, as might be expected, because dehydroxylation of dioctahedral micas typically enhances the exchangeability of interlayer K. Also, as was observed with the 0.2-2 μm and <2 μm muscovite samples, the increases in K release rate stopped in the Tumut sample well before the dehydroxylation reached completion. This behavior stems from the overly long extraction period that was used for the rate index in small particles rather than a distinctive property of the mineral. Another similarity in the <2 μm Tumut and muscovite results can be seen in the breadth of the maxima of the release rate curves. These maxima are much broader than that of coarse muscovite because the smaller particles responded to lower temperatures.

On the other hand, major differences in the <2 μm Tumut and muscovite results occurred because no progressive reduction in K release took place as the temperature was increased to 750°C. These differences are reflected in the initial rate and maximum release curves and can be attributed to the lack of layer weathering in the Tumut sample. Instead of decreasing, the 1-minute K release values actually increased and at temperatures where only edge weathering and dehydroxylation effects could be involved. The release rate (3-hour data) increased slightly at temperatures of 300 to 400°C, which were too low for dehydroxylation. This effect

of thermal treatments will be discussed later with comparable results that were obtained with mica-vermiculite samples.

When the Tumut samples were heated at temperatures about 750°C, the rate and maximum degree of K release decreased in a manner and to an extent that was more like the 10-20 μm than the <2 μm ground mica. Mineral alterations due to extensive grinding must have made the particles more sensitive to high temperatures. Since the <2 μm muscovite and Tumut particles had a similar size, this difference must lie in the edge alterations that also produced the different degrees of layer weathering.

Whereas the <2 μm Tumut and ground muscovite samples were essentially 10 Å materials, most fine-grained micaceous minerals in soils and sediments have a mixed-layer structure. The effects of mixed layering, therefore, had to be considered in this study of thermally treated minerals. This was done with samples of <2 μm Grundite illite, which has 10 Å mica layers randomly interstratified with expanded layers. According to Gaudette et al. (1966), 25 to 30% of the layers in Grundite are expanded. Actually, the idea of using thermal treatments to study interlayer K exchangeability was first applied to Grundite samples (Smith and Scott, 1963). Additional experiments were carried out with heated Grundite in a comparison of several fine-grained,

micaceous minerals (Smith and Scott, 1974) but many more thermal treatments had to be applied to the $<2\ \mu\text{m}$ Grundite samples to determine the relative behavior of $<2\ \mu\text{m}$ particles of Tumut, Grundite and muscovite.

The curves in Fig. 22 describe the K release that occurred when $<2\ \mu\text{m}$ Grundite samples were heated for 24 hours at selected temperatures and were extracted with NaCl-NaTPB solutions for different periods. It is evident from these results that the response of the Grundite to thermal treatments was similar to that of Tumut, not muscovite. With temperatures up to 700°C , the only differences between the Grundite and Tumut release curves are those stemming from the particle sizes in the two $<2\ \mu\text{m}$ samples. Due to a greater abundance of very small particles, the Grundite samples released much more K in the initial extraction period and had a lower maximum degree of release.

When small particles of micaceous minerals are degraded in NaCl-NaTPB solutions, the rate of K release by edge weathering can be rapid enough to obscure any evidence that layer weathering occurred. The effects of thermal treatments on the initial release of K, however, can help identify the occurrence of layer weathering. As shown with ground mica samples (Fig. 14), an initial release of K that is due to layer weathering is reduced by thermal treatments. The initial release of K by $<2\ \mu\text{m}$ Tumut samples, on the other

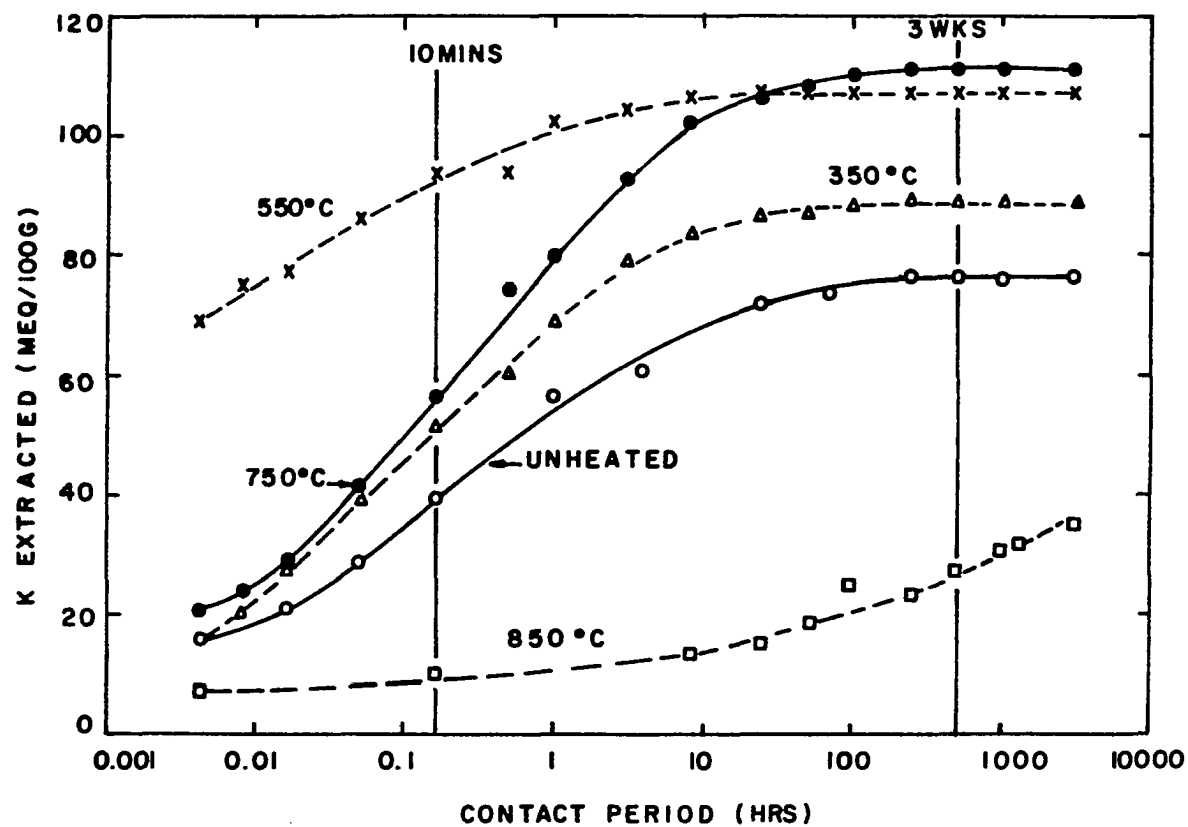


Fig. 22. K extracted from $<2 \mu\text{m}$ Grundite illite samples that were heated at different temperatures for 24 hours, then placed in NaCl-NaTPB solutions for different periods

hand, was attributed to edge weathering because the amount of release was increased by temperatures that caused dehydroxylation. The amounts of K extracted from $<2\text{ }\mu\text{m}$ Grundite samples in extraction periods of only 15 seconds were also increased by various heat treatments. These results and the shape of the K extraction curves indicate that the naturally-occurring Grundite particles do not release K by layer weathering. This similarity between the Tumut and Grundite means the presence of mixed layering is not a relevant factor. More important, the lack of layer weathering in both samples of $<2\text{ }\mu\text{m}$ illite raises questions as to why the Grundite sample releases a smaller fraction of its K. Explanations of the small particle effects in terms of layer weathering should be restricted henceforth to ground mica samples.

Increases in the maximum degree of K release were achieved with heated samples of both illites, but the lower maximum value for the unheated Grundite (66% versus 86% for Tumut) permitted more increase in the heated Grundite samples. Even with heated samples, the maximum levels of K release did not exceed 96% and 97% for the Grundite and Tumut samples, respectively. When the heating temperature was raised to 750°C , the rate of release was reduced but not the maximum level of release. Higher temperatures reduced the release rate so much that there is no way of knowing

from the 3-week extraction period whether a reduction in maximum release occurred or not.

Samples of $<2\ \mu\text{m}$ Grundite illite were heated at temperatures of 110 to 950°C for 24 hours and placed in NaCl-NaTPB solutions for 3 weeks and 10 minutes to determine the maximum degree of K release and the rate of K release, respectively. These results and the weight loss by the heated samples are presented in Fig. 23. The Grundite response to thermal treatments was very comparable to that of Tumut illite and provided no evidence that the mixed layering played a role in the exchange of interlayer K. Decreases in both the release rate and the maximum levels (measured by 3-week extraction periods) occurred at slightly lower temperatures in the Grundite samples. This difference may be due in part to the presence of smaller particles in the Grundite sample, but the 850°C curve in Fig. 22 shows the 3-week extraction periods may have been too short to give a true measure of the maximum levels of K release in the high temperature, illite samples.

Grundite samples that were heated at temperatures of 200 to 300°C exhibited a slight increase in rate of K release instead of the decrease that was observed with $<2\ \mu\text{m}$ muscovite. This response of the Grundite illite to thermal treatments and a similar response of the Tumut illite will be discussed with the mica-vermiculite data.

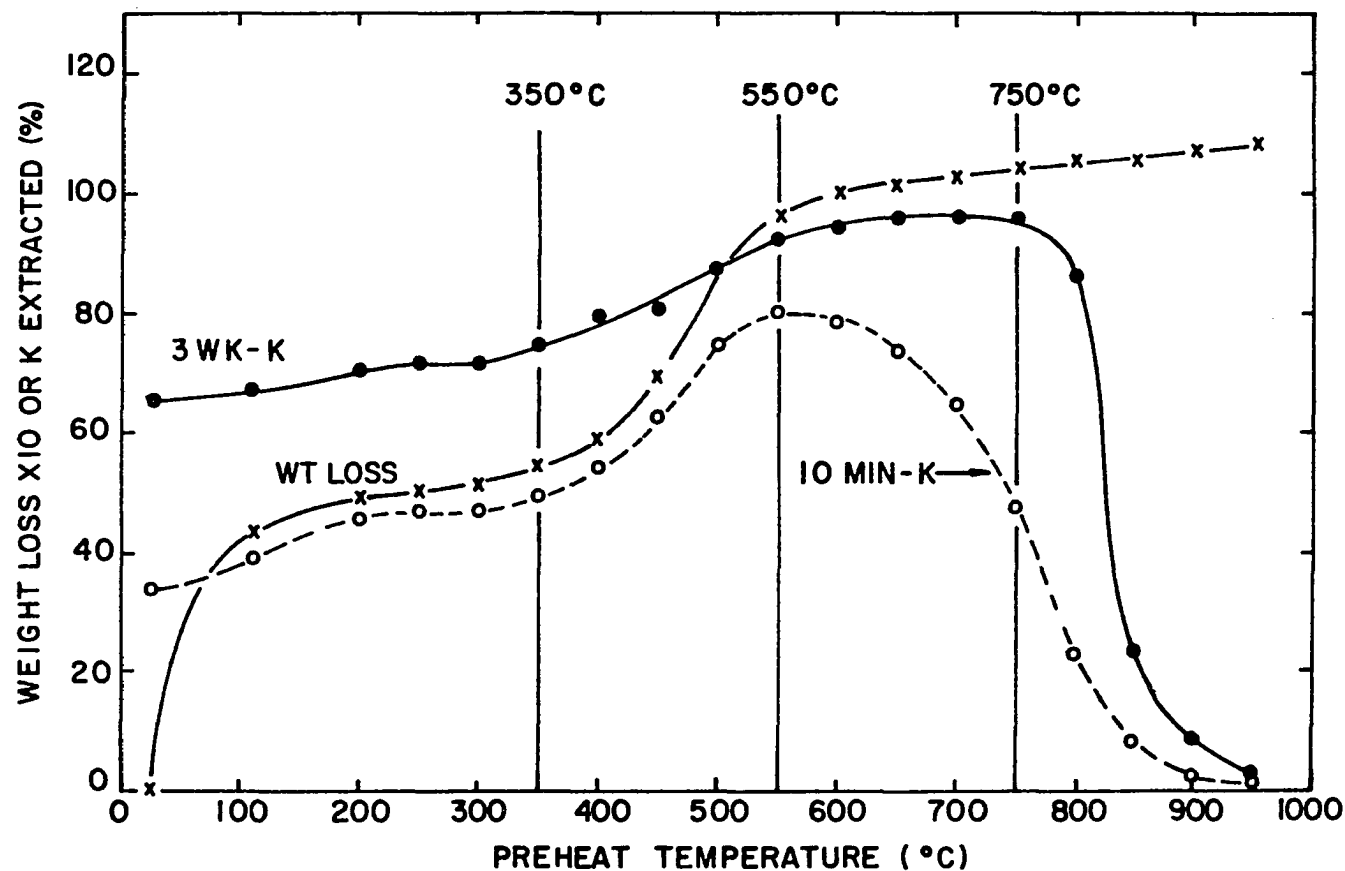


Fig. 23. Weight loss by $<2 \mu\text{m}$ Grundite illite samples that were heated at different temperatures for 24 hours and K extracted by placing the heated samples in NaCl-NaTPB solutions for 10 minutes and 3 weeks

A major consequence of there being expanded layers in the Grundite particles is the presence of large amounts of sorbed water in the mineral. As shown by Fig. 21 and 23, there was about 1.5 and 5% hydration water in the $<2\ \mu\text{m}$ Tumut and Grundite illites, respectively. Some of this difference in sorbed water could be due to the presence of more small particles in the Grundite sample, but a removal of this water by low heating temperatures should have caused some alteration in the K release data if mixed layering were a significant factor in interlayer K exchange. No relationships of this type were observed.

On the other hand, an increase in the heating temperature to 350°C initiated dehydroxylation and an associated increase in K exchangeability in the Grundite sample. The longer the sample was heated at 350°C the greater was the rate and maximum degree of K release (Fig. 24 and 25). This response of $<2\ \mu\text{m}$ Grundite to 350°C differs markedly from the reduction in K exchangeability observed with 350°C -heated $<2\ \mu\text{m}$ muscovite because changes in edge weathering rather than layer weathering were involved. Other effects of different heating periods on the weight loss and K release by Grundite illite are shown in Fig. 24 and 25, but describe nothing unusual about this mixed-layer illite. From the standpoint of using thermal treatments to maximize the degree of K release by Grundite samples in NaCl-NaTPB solutions, it

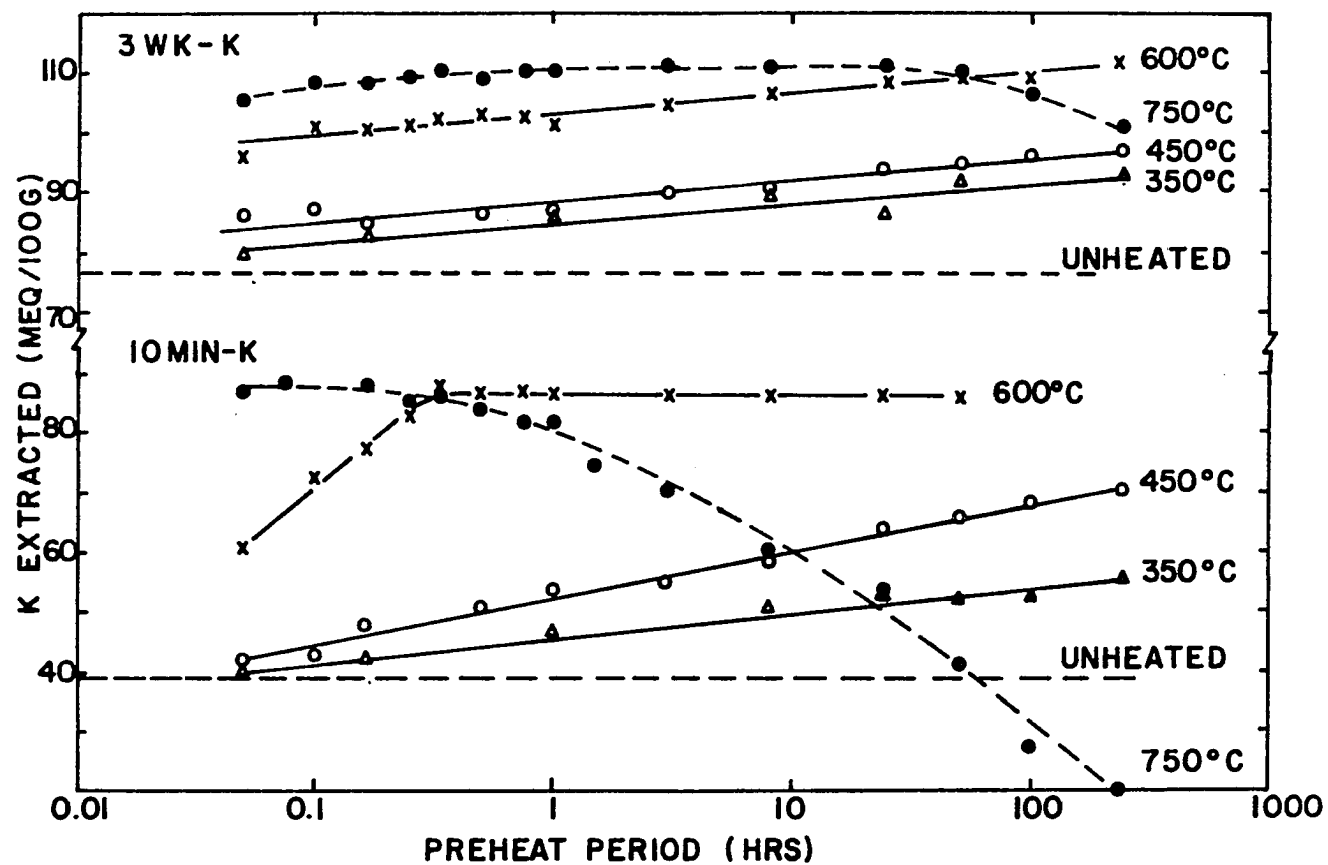


Fig. 24. K extracted from $<2 \mu\text{m}$ Grundite illite samples that were heated at different temperatures for different periods, then placed in NaCl-NaTPB solutions for 10 minutes and 3 weeks.

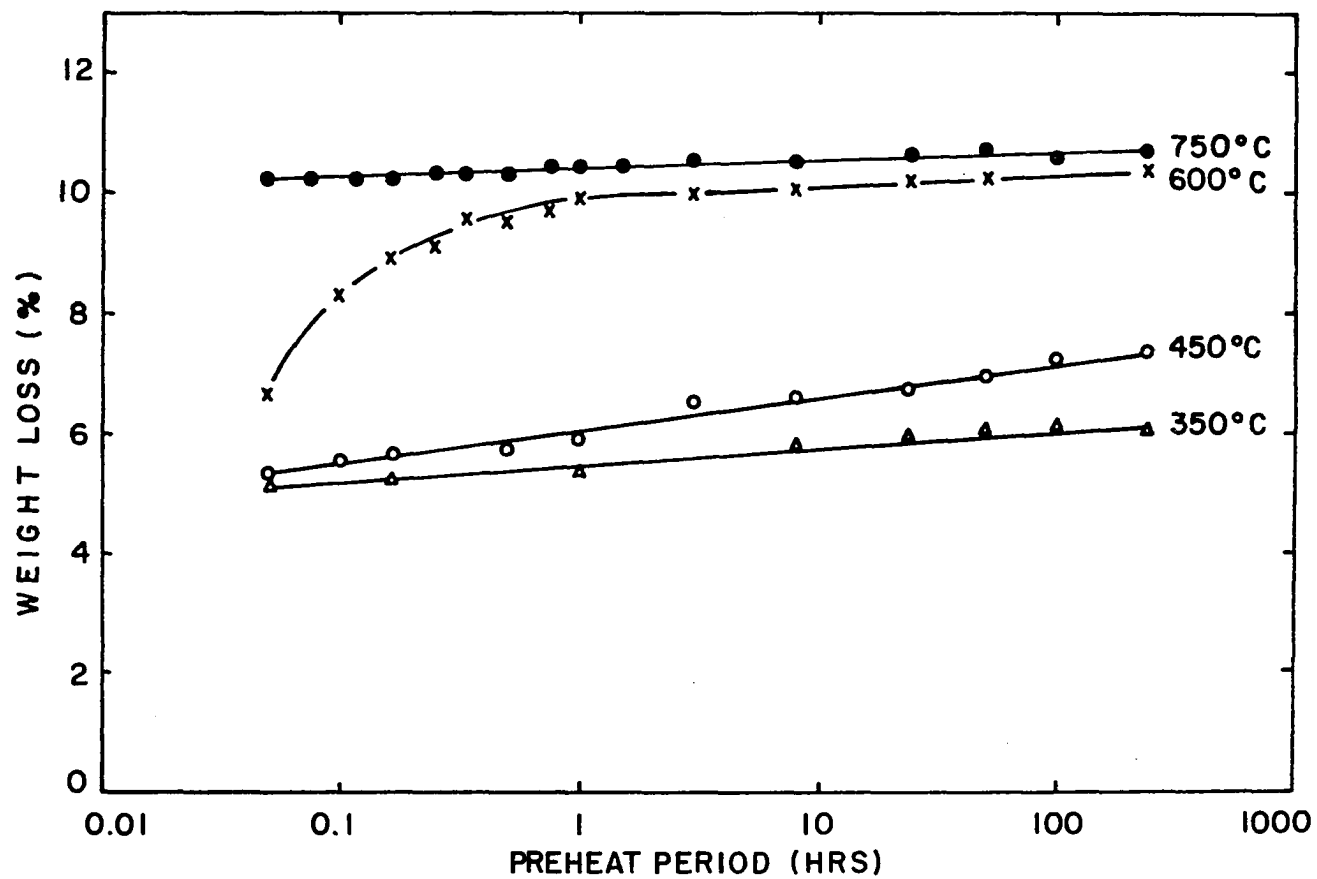


Fig. 25. Weight loss by $<2 \mu\text{m}$ Grundite illite samples heated at different temperatures for different periods

should be noted that prolonged heating periods at high temperatures can be detrimental. Actually, the extraction of 111 meq K/100 g from the samples heated at 750°C for 3 hours or 600°C for 10 days represents 96% of the total and probably all the interlayer K because this illite sample contains some feldspar particles.

D. Mica-vermiculites

When Scott et al. (1972) heated biotite, lepidomelane and fluorphlogopite samples and Kozak (1976) made a detailed study of the response of lepidomelane to heat treatments, only reductions in K exchangeability were observed. This consistent observation with trioctahedral minerals contrasted sharply with the increased rates of K release observed with dioctahedral muscovite and was construed as being the result of a distinctive difference in the mineral parameters governing K release in the two mineral groups. Preliminary experiments with heated <50 μm samples of the SCH mica-vermiculite used in this investigation (Scott et al., 1972), however, did not support this concept in that they behaved more like the dioctahedral minerals in having an enhanced K exchangeability even though the mineral was trioctahedral. To reconcile these observations, further work with mica-vermiculites was obviously needed.

Samples of four mica-vermiculites were subjected to

various heat treatments. As shown by their K contents, 55, 107, 75, and 197 meq K/100 g in the SCH, SCL, MH, and ML samples, respectively, these samples differed in their content of contracted mica layers. Whereas the ML mineral was essentially all biotite, the SCH mineral was nearly 75% expanded. Thus, these samples ranged from the SCH mineral that behaved like dioctahedral micas when heated to the ML mineral that should behave like trioctahedral biotite.

Since the mica-vermiculite minerals release their K to NaCl-NaTPB solutions very rapidly--only an hour being needed for complete K release by <50 μ m SCH samples in experiments by Scott et al. (1972)--they were very coarsely ground to <1/16" for this study. As shown in Fig. 26, these coarse particles released their K slowly enough that their release curves should provide visible responses to thermal alterations. The 30-minute and 3-week extraction periods are marked on these curves to show the points at which the rates and maximum degrees of K release were measured.

From the 3-week data in Fig. 26, it is evident that the coarse mica-vermiculite samples did not release all their K to the NaCl-NaTPB solutions. Only 98, 93, 68, and 87% of the K in the SCH, SCL, MH, and ML samples, respectively, proved to be exchangeable. Whether this behavior of the coarse mica-vermiculite particles can be related to the limited K release in small particles of muscovite and illite

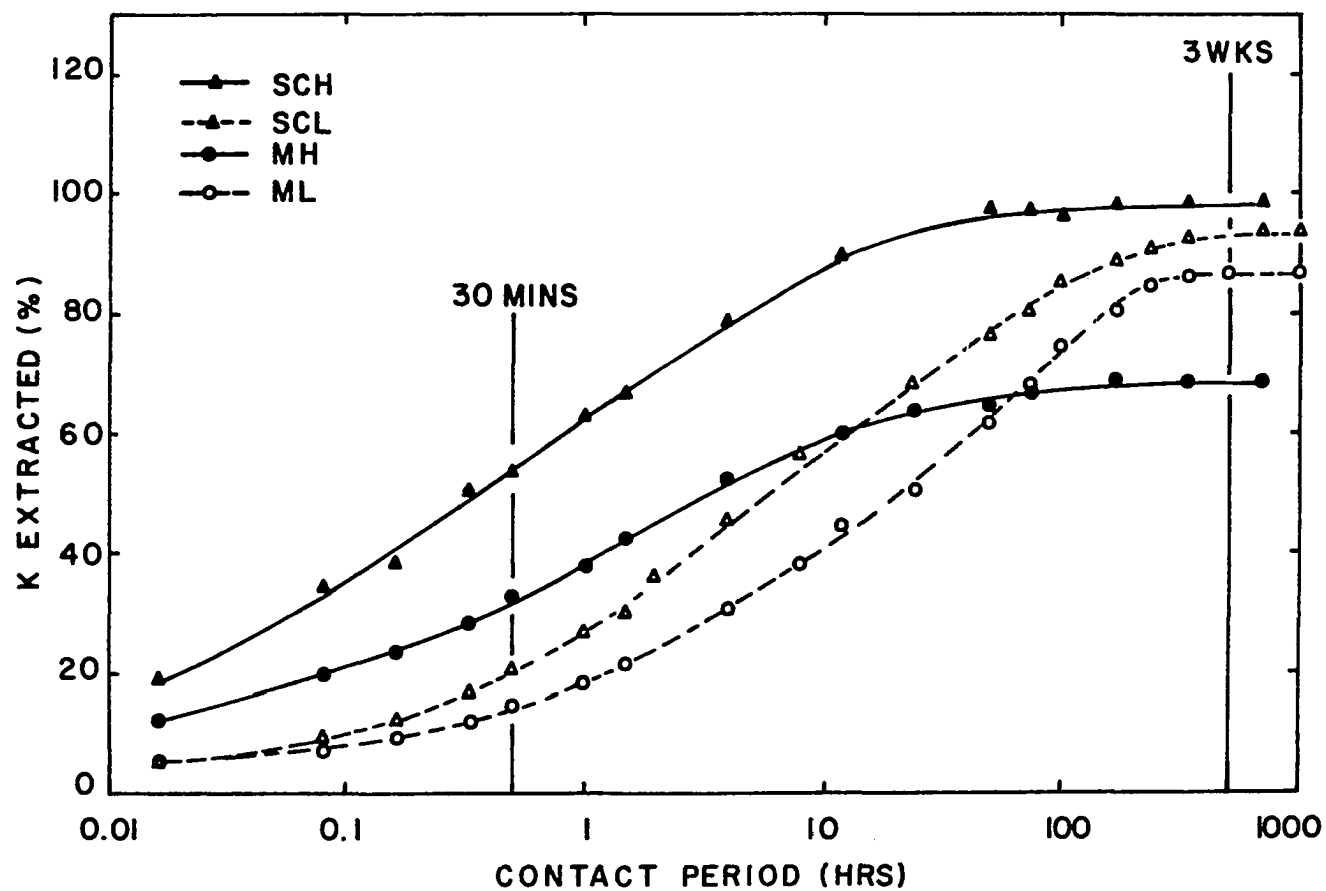


Fig. 26. K extracted from SCH, SCL, MH, and ML mica-vermiculite samples that were placed in NaCl-NaTPB solutions for different periods

and attributed to the presence of expanded layers is not entirely clear. Certainly there were expanded layers in the mica-vermiculite samples from the beginning of the extraction period, but estimates of the degree of mixed layering based on the K content of the minerals do not correlate with the maximum levels of K release. Many of the open layers, of course, may be located in the vermiculite component of the mineral and not in positions next to contracted layers of hydrobiotite where they could influence the release of K. Also, the mica-vermiculites may be more susceptible to layer weathering than dioctahedral minerals and have the maximum degree of K release limited by newly opened layers even in coarse particles. Since the MH sample has about 60% expanded layers and only 68% extractable K, it appears to be a particularly good sample for further work on the limited degree of K release in mica-vermiculites.

It is evident from the four K release curves in Fig. 26 that the rates of K release (the slope of the curves) varied with the mineral and with the degree of K release in each mineral. Thus, to compare the minerals in regard to their K release rates and to determine the effects of thermal treatments on these rates, the amount of K released in 30 minutes was determined and used as an index of the K release rate in each sample. Obviously, these measurements do not describe the rate with which any segment of K is re-

leased, but they do reflect the occurrence of faster or slower release rates and can be discussed in these terms. The results obtained with samples of the mica-vermiculites that were heated for 24 hours at different temperatures and then extracted with NaCl-NaTPB solutions for 30 minutes are presented in Fig. 27.

The SCH and SCL samples and, to a lesser extent, the MH samples exhibited an increase and then a decrease in K release when the heating temperature was increased from 450°C to about 600°C and then to 850°C. These results verify the earlier observation of Scott et al. (1972) that thermal treatments can enhance the exchangeability of K in both trioctahedral and dioctahedral micaceous minerals. On the other hand, the ML mineral behaved like biotite by exhibiting only a decrease in K release when it was heated in this temperature range. While there was no increase in K exchangeability in the heated ML samples that had little mixed layering, no consistent relationship between the degrees of K release and mixed layering were observed. The mixed layering in the mica-vermiculites did not account for the differences in the lower temperature alterations in the minerals either. When the samples were heated at temperatures of 25 to 400°C, the ML again behaved like biotite by undergoing no change in K release, whereas the other mica-vermiculite exhibited different degrees of change. In no case did these minerals

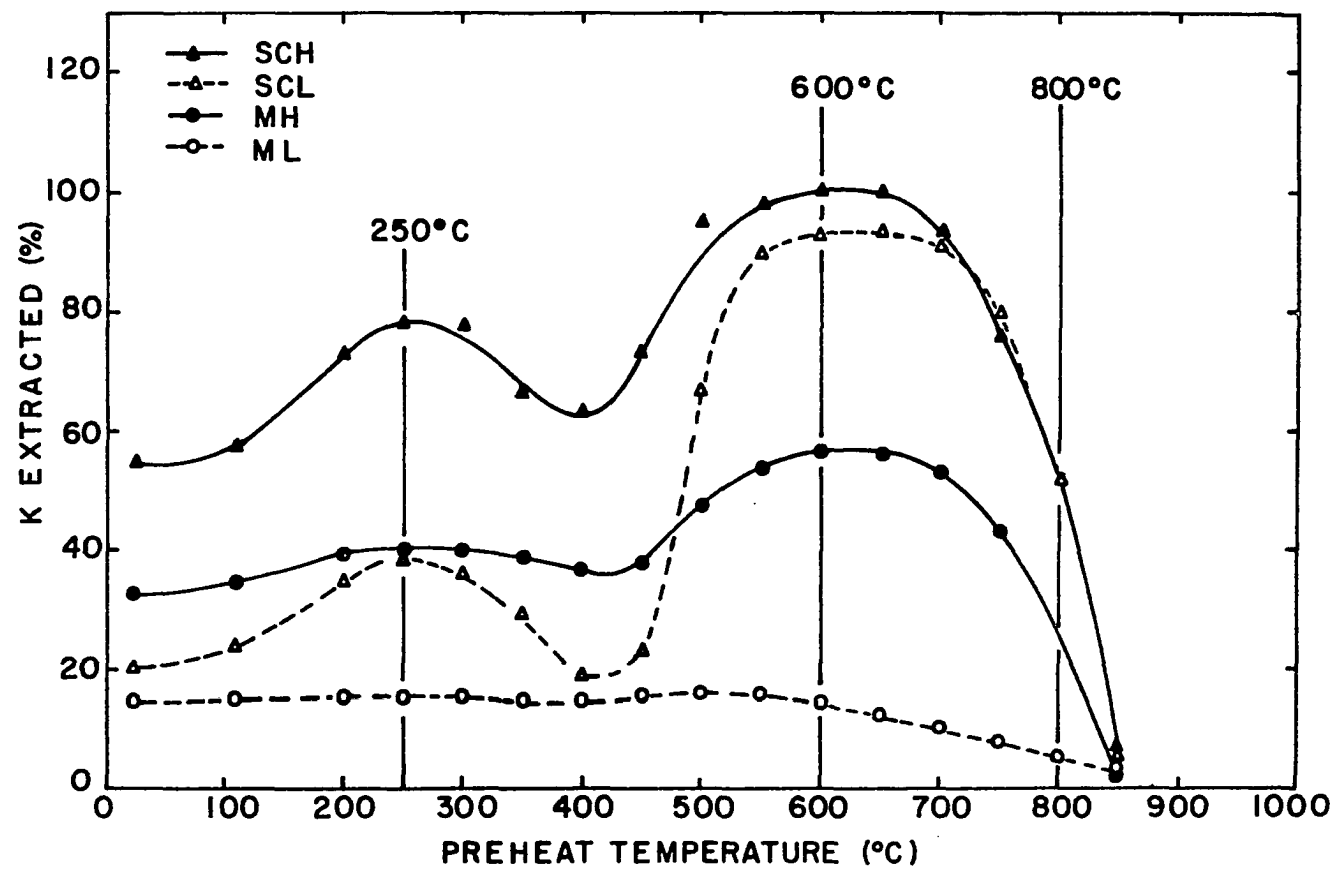


Fig. 27. K extracted from SCH, SCL, MH, and ML mica-vermiculite samples that were heated at different temperatures for 24 hours and then placed in NaCl-NaTPB solutions for 30 minutes

behave like ground muscovites in that their K release rate did not decrease progressively as the heating temperature was increased. Instead, the SCH and SCL minerals released more K after being heated at 250°C than they did after higher or lower heating temperatures. Explanations for these complex changes in the K release rates of the heated minerals and for the differences in the mineral responses to the thermal treatments are not provided by the data in Fig. 27. Thus, more detailed studies were carried out with selected samples of heated mica-vermiculite.

The effects of selected thermal treatments on the exchangeability of K in SCL samples are described by the curves in Fig. 28. These results were obtained with samples that were unheated or heated at different temperatures for 24 hours and then extracted in NaCl-NaTPB solutions for different periods. From the K release curves, it is evident that all the heat treatments enhanced the rate of release and caused relatively little change in the maximum degree of release. When the SCL samples were heated at 600°C for 24 hours, both the initial K release and the rate of K release were greatly enhanced. As a result, nearly all the K in the mica (93%) was extracted from the 600°C samples in a 1-hour period. On the other hand, the 800°C treatment produced a small decrease in the maximum degree of K release, a decrease in the initial K release and a smaller increase in the rate of K

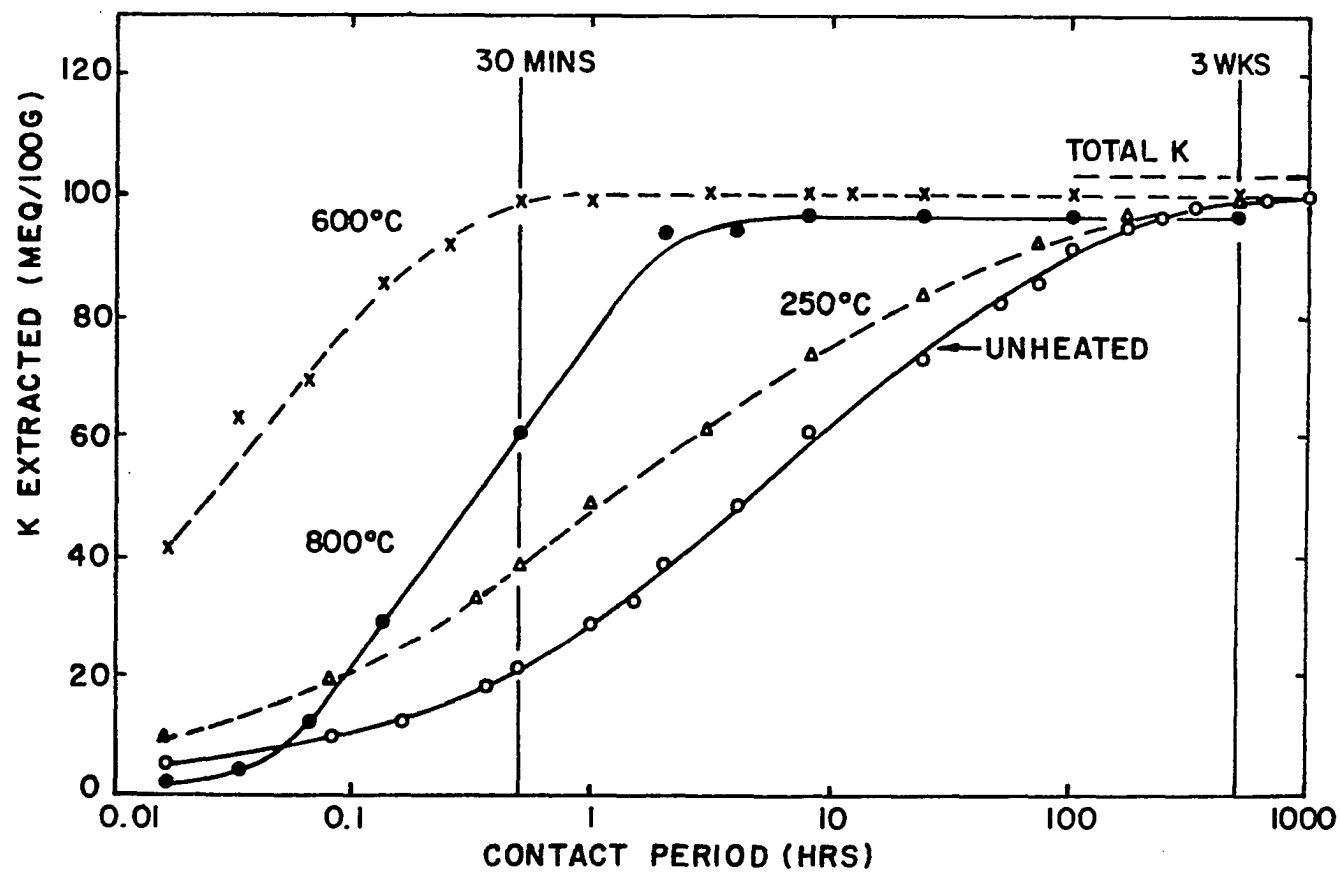


Fig. 28. K extracted from SCL mica-vermiculite samples that were heated at different temperatures for 24 hours, then placed in NaCl-NaTPB solutions for different periods

release. It is evident from these increases in K exchangeability that this mineral behaved more like a dioctahedral than a trioctahedral mineral when it was heated. Even though the SCL particles were quite coarse, their response to thermal treatments, especially the 250°C temperature, was comparable to that of fine-grained illite rather than muscovite. The samples heated at 250°C exhibited an increase (not a decrease like the muscovite size-fractions) in the exchangeability of all the extractable K as did the 350°C Grundite samples. This similarity of the SCL and Grundite samples probably stems from the presence of mixed layering in both minerals.

Additional effects of thermal treatments on the weight loss and the rate and the maximum degree of K release by SCL samples are shown in Fig. 29. Weighed samples of the SCL mineral were heated at different temperatures for 24 hours, weighed again to determine their weight loss and then placed in NaCl-NaTPB for selected periods. The extraction periods of 30 minutes and 3 weeks were used to determine the rate and maximum degree of K release, respectively.

The 3-week K curve shows the heat treatments had no effect on the maximum degree of K release until the heating temperature exceeded 750°C. Higher temperatures produced a sharp decrease in the maximum amount of K release. Relatively little information is available on the effects of

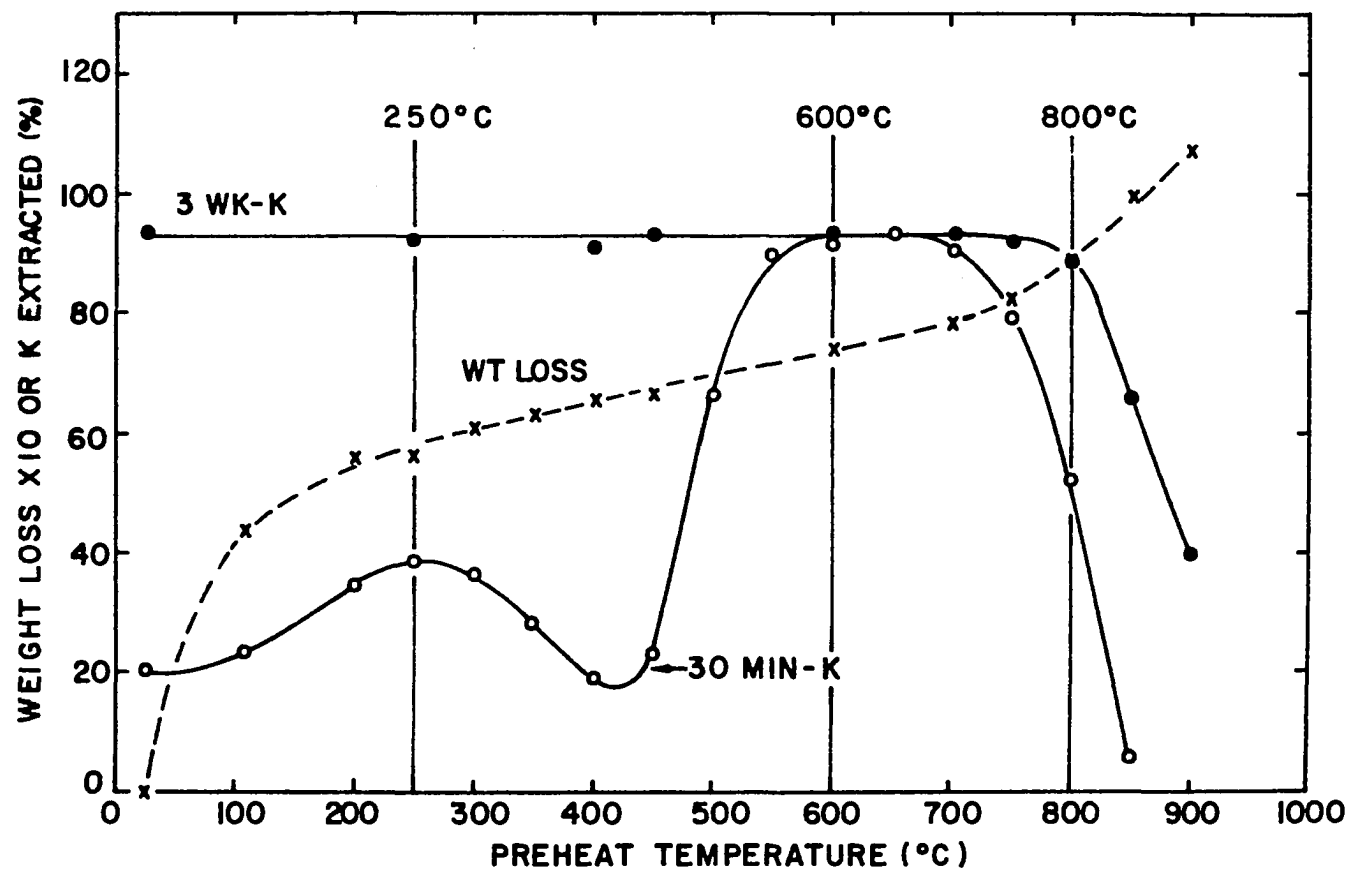


Fig. 29. Weight loss by SCL mica-vermiculite samples that were heated at different temperatures for 24 hours and K extracted by placing the heated samples in NaCl-NaTPB solutions for 30 minutes and 3 weeks

high heating temperatures on the maximum release by trioctahedral micas, but phlogopite, at least, did not give this response at 850°C (Kozak, 1976). On the other hand, the fine-grained dioctahedral illites (Fig. 21 and 23) did release less K after they were heated at temperatures above 750°C. Thus, once again the SCL mineral behaved more like dioctahedral than trioctahedral minerals and gave indications that small particle sizes and mixed layering may be involved.

The 30-minute K curve in Fig. 29 shows the magnitude of the increase in K release rate that occurred when the heating temperature was increased to about 250°C. As shown by the weight loss curve, these heat treatments removed most of the hydration water in the mineral. Some of this water is located in interlayer positions in mica-vermiculites and can cause exfoliation if it is removed suddenly by heat treatments. Any exfoliation that did occur in the 250°C samples did not expose much interlayer K to immediate exchange because the 1-minute K value for the 250°C curve in Fig. 28 is quite low. Instead, the dehydration and possibly the exfoliation of this mineral enhanced the exchangeability of K in the contracted portion of the mineral. When the heating temperature was increased from 250 to 400°C, this heating effect either decreased or was overshadowed by other thermal effects which reduced the K exchangeability.

Mixed layering seems to be involved in the low tempera-

ture response of the SCL mineral because no such response occurred in the ML mineral (Fig. 27), which has little or no mixed layering. This idea is supported by the observation that samples of Grundite, which has considerable mixed layering, responded to the low temperature treatments like the SCL mineral rather than the contracted muscovite samples. The apparent degree of mixed layering, however, does not appear to be the only factor since the MH mineral has much more mixed layering than the SCL mineral but much less response to the 250°C heating. Moreover, the Tumut illite, which has essentially no mixed layering, exhibited an increase in K release rate (instead of decrease like the muscovite samples) when the mineral was heated at these low temperatures. Particle size was not a factor because the four mica-vermiculites were alike in regard to their particle size but different in their low temperature response.

When the heating temperature was increased from 400 to 600°C or 650°C and then to 850°C, the K release rate increased and decreased very like the 10-20 µm muscovite. However, the sharp increase in the release rate of the SCL mineral cannot be attributed to a dehydroxylation of the mineral as it was in muscovite. A graduate weight loss did occur in the SCL mineral as the temperature was increased from 250 to 800°C, but the weight loss curve provided no variations that can be related to dehydroxylation or the increase in K release rate.

Since the rate increase depicted by the SCL curve from 400 to 600°C did not occur in the ML mineral, the presence of mixed layering again may be involved, but the mechanism of this change is not clear.

Relative to the other mica-vermiculites, the MH mineral released the smallest fraction of its total K (68%) but was otherwise intermediate in its properties, especially its degree of mixed layering. Thus, complete K release curves were determined with selected samples of heated MH mineral and examined for any unusual responses to thermal treatments. The results in Fig. 30 show the rate of K release in the 600°C-heated MH samples was increased but both the initial K release and maximum degree of K release were not changed. Like the 800°C samples of SCL mineral, the 800°C samples of MH exhibited a lower initial and maximum degree of K release but a higher rate of K release by edge weathering. The rate of K release in the heated MH samples seemed to be slower than the heated SCL samples--10 hours being needed to extract the maximum extractable K from the MH samples versus 30 minutes for the SCL samples. In general, the effect of thermal treatments is not so pronounced in MH samples as in SCL samples.

Additional experiments were carried out with the ML mineral because it differed from the other mica-vermiculites by having more structural Fe, less mixed layering and a

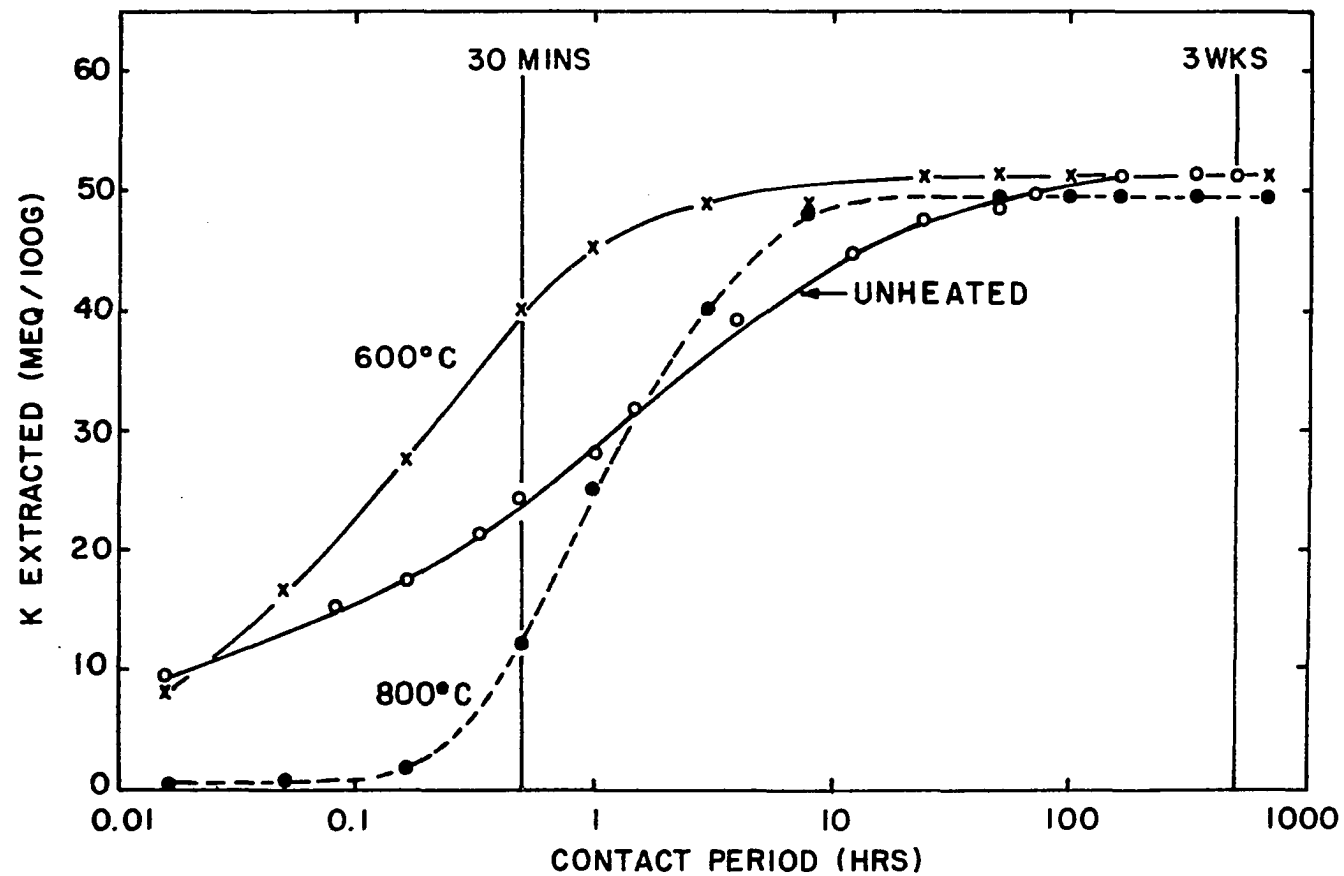


Fig. 30. K extracted from MH mica-vermiculite samples that were heated at different temperatures for 24 hours and then placed in NaCl-NaTPB solutions for different periods

unique response to a range of heating temperatures. The results are presented in Fig. 31 and 32.

The data in Fig. 31 were obtained by heating ML samples at 450 or 600°C for 24 hours and then extracting the K with NaCl-NaTPB solutions for 24 hours. There were only slight changes in the K release rate and no changes in the initial and the maximum amount of K release when these thermal treatments were used. This behavior of the heated ML samples contrasts sharply with the major increases in K exchangeability exhibited by heated samples of SCL (Fig. 28), MH (Fig. 30) and SCH (Scott et al., 1972) samples. The ML samples also differ from the other mica-vermiculites by having much less mixed layering and a higher K content. In terms of these properties, the ML mineral seems to be comparable to biotite and, as such, should give a thermal response like biotite instead of the mica-vermiculites. However, heating experiments with biotite (Scott et al., 1972) and with lepidomelane (Kozak, 1976) have made it clear that the exchangeability of K in these trioctahedral micas is greatly reduced by similar temperatures. Thus, the response of the ML samples to heat treatments was not like that of mica-vermiculite or biotite.

The biotite used by Scott et al. (1972) and the lepidomelane used by Kozak (1976) contained large amounts of ferrous iron (242 and 258 mmoles Fe^{++} /100 g, respectively)

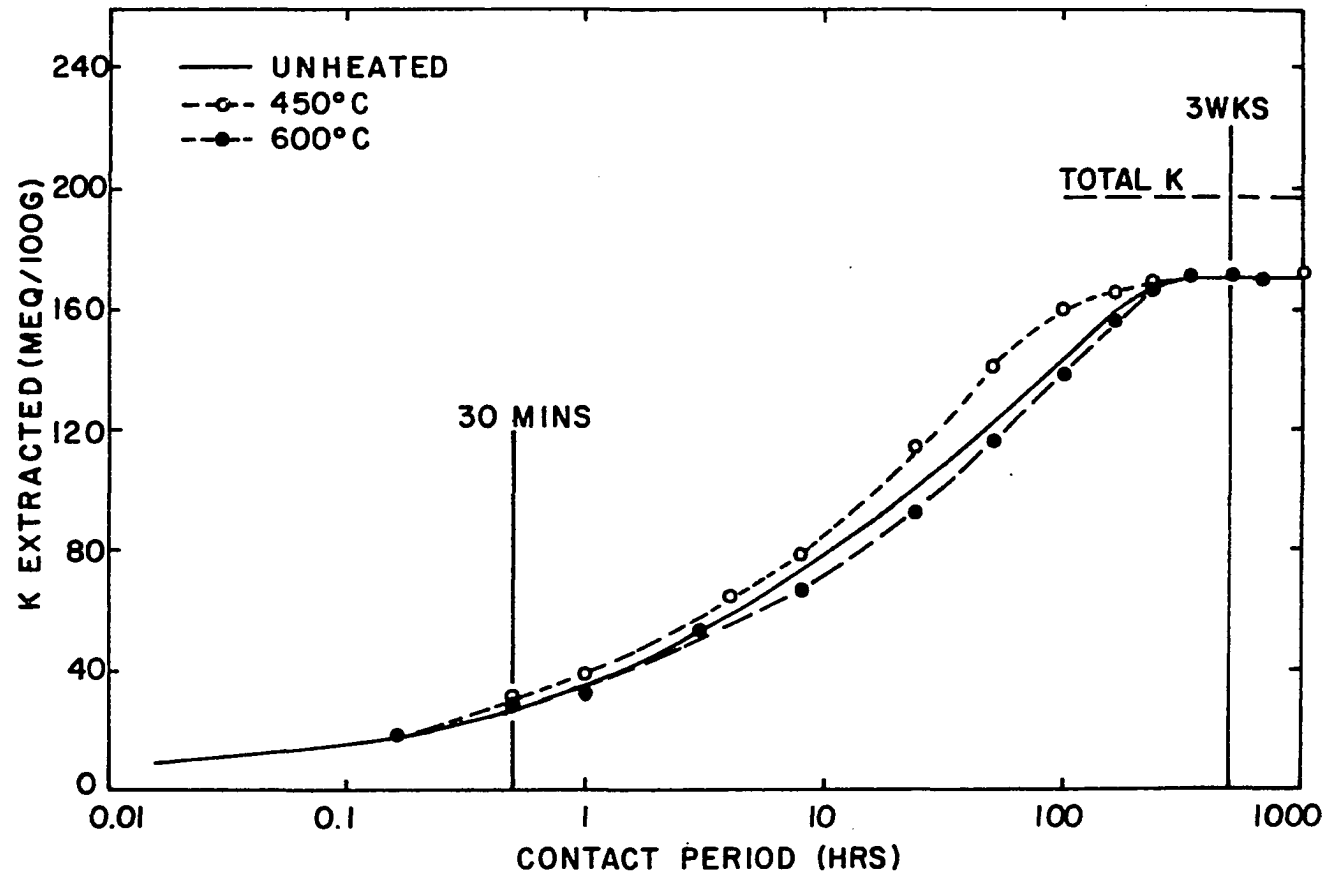


Fig. 31. K extracted from ML mica-vermiculite samples that were heated at different temperatures for 24 hours and then placed in NaCl-NaTPB solutions for different periods

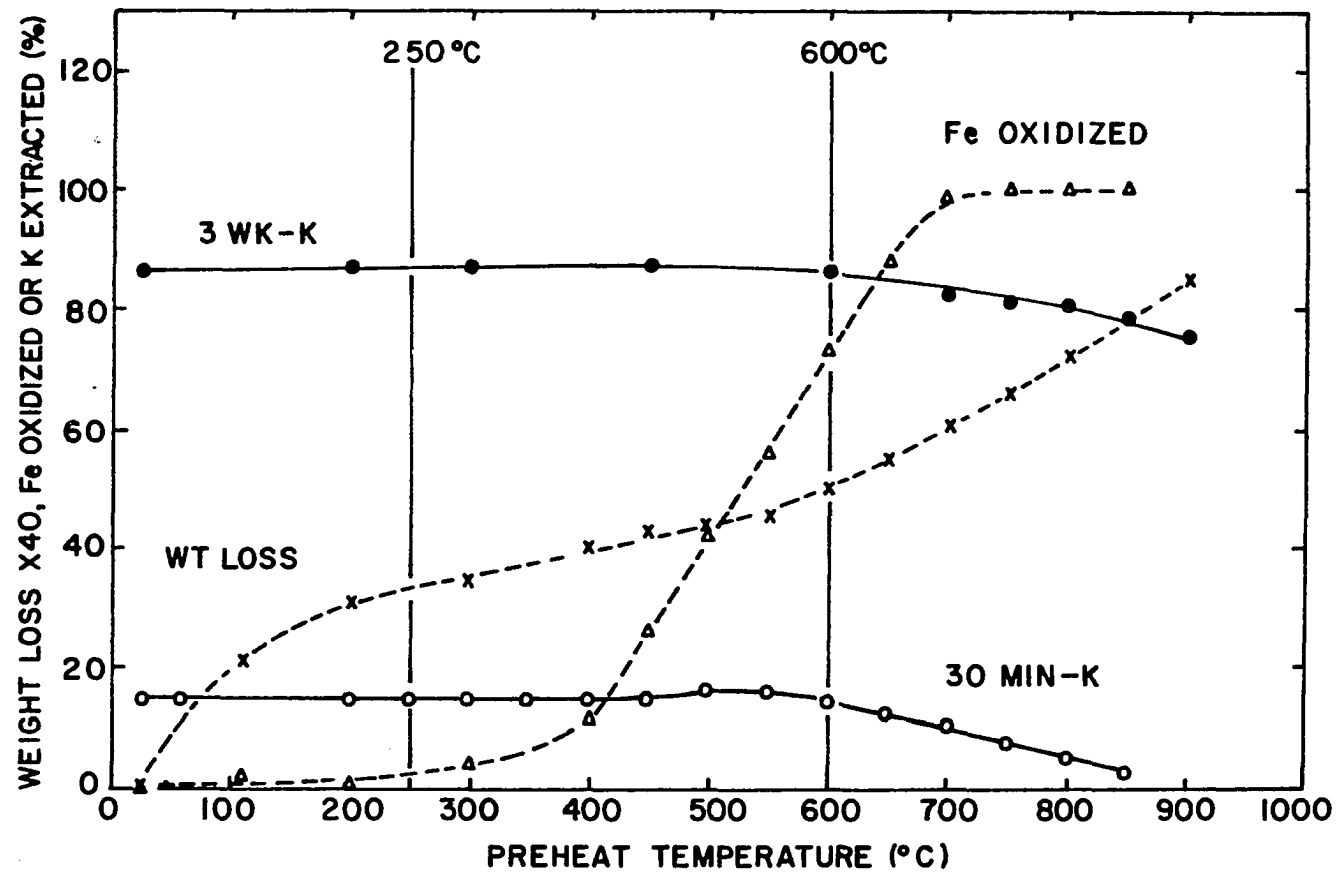


Fig. 32. Weight loss and Fe^{++} oxidation by ML mica-vermiculite samples that were heated at different temperatures for 24 hours and K extracted by placing the heated samples in NaCl-NaTPB solutions for 30 minutes and 3 weeks

which have been credited with causing the reduction in K exchangeability in heated samples. When these trioctahedral micas are heated, oxidation of this Fe^{++} occurs and the mineral is altered by the accompanying processes of deprotonation, Fe ejection, etc. As a result, the interlayer K in the oxidized biotite can interact more strongly with the residual oxygens and offer more resistance to exchange. Thus, the importance of Fe^{++} in the ML mica-vermiculite had to be considered.

Total Fe and Fe^{++} determinations were carried out with all the mica-vermiculites. Values of 11, 17, 11 and 91 mmoles $\text{Fe}^{++}/100$ g and of 112, 113, 103, and 122 mmoles total Fe/100 g were obtained for the SCH, SCL, MH, and ML samples, respectively. Obviously, the ML mineral contained more Fe^{++} than the other mica-vermiculites and enough to be a potential factor in heated samples. Samples of the ML mineral, therefore, were heated at different temperatures for 24 hours and characterized in terms of Fe^{++} oxidation, weight loss and K exchangeability. Extraction periods of 30 minutes and 3 weeks were used to determine the rates and maximum degrees of K release in the various samples. The results of this experiment are presented in Fig. 32.

Little change in the rate of K release or the maximum degree of K release occurred when the ML samples were heated at temperatures up to 600°C . Higher temperatures reduced the

exchangeability of K to some degree but even the 850°C treatment did not have much effect. This behavior of the ML mineral is quite unlike that of biotite. Moreover, the role of Fe^{++} in the two minerals appears to be different. Fe^{++} oxidation started to occur at temperatures as low as 300°C as it did in biotite, but the inverse relationship between Fe^{++} oxidation and K exchangeability reported by Kozak (1976) for mica was not observed. Instead, most of the Fe^{++} was oxidized before a change in K exchangeability occurred in the ML mineral. Since there was only 91 mmoles Fe^{++} /100 g in the ML mineral, it is conceivable that the Fe^{++} distribution was too diffuse to have an impact on the K in oxidized samples. This possibility should be evaluated with a group of biotite samples that range from phlogopite to lepidomelane in regard to their Fe^{++} content.

The weight loss curve for the ML mineral (Fig. 32) is typical for trioctahedral micas. Only a weight loss due to dehydration at the low temperatures is particularly evident. The changes in weight that did occur at progressively higher temperatures had no visible impact on the exchangeability of K in the mineral.

V. SUMMARY AND CONCLUSIONS

When micaceous minerals are exposed to aqueous solutions a release of interlayer K occurs. This release of K plays a significant role in the weathering of micas and the utilization of K by growing plants. Thus, the processes and factors governing the release of interlayer K have been studied extensively. This investigation has focused on the release of K that occurs by an ion exchange mechanism.

It is known that the exchangeability of interlayer K is governed by the conditions imposed by the solution around the mineral particles and the properties of the minerals themselves. Details on many of these complex and interacting effects of the solutions and minerals, however, have not been resolved. In particular, the role of mineral properties is unclear because the exchange process is often dominated by conditions outside the mineral particles. To reverse this situation, laboratory experiments were carried out with procedures that controlled the effects of the solution phase and related the exchangeability of K to characteristics of the mineral. A dual approach was used in that the exchangeability of K in several micaceous minerals was related to differences in existing properties of the minerals and to thermally induced changes in these properties. It was proposed that these relationships could be used to ascertain the role of mineral properties in the exchange of interlayer K.

Various thermal treatments were applied to samples of muscovite and related micaceous minerals that differed in regard to their particle size and mixed layering. The heated minerals were examined for changes in their K exchangeability and associated mineral alterations. The investigation was confined to minerals that would provide information about the increases and decreases in K exchangeability encountered with heated muscovite. The emphasis, therefore, was on dioctahedral minerals. Some trioctahedral mica-vermiculites were included because their response to thermal treatments provided a link between the dioctahedral and trioctahedral mineral behavior.

One-half gram samples of the various minerals were heated in an unvented oven or furnace for specified periods at different temperatures. The heated samples were then placed in a NaCl-NaTPB solution at 25°C for selected periods to determine the exchangeability of their interlayer K. Complete K extraction curves were obtained with some heated samples, whereas, other samples were characterized by their initial release of K (shortest extraction period), their maximum level of extractable K and their rates of K release. The amounts of K extracted by selected extraction periods were used as arbitrary indices of the release rate. Each sample was weighed before and after it was heated and the weight loss was construed as a measure of the water lost by

dehydration or dehydroxylation in the mineral. The basic effects of the heat treatments on K exchangeability in dioctahedral micas were first established with coarsely ground muscovite samples. The effects of particle size on this thermal response were then determined with various size-fractions of ground muscovite. Using the results for a $<2\text{ }\mu\text{m}$ ground muscovite sample as a reference, comparisons were made with the thermal responses of $<2\text{ }\mu\text{m}$ fractions of two naturally-occurring illites to determine the effects of mineral grinding and mixed layering on the exchangeability of interlayer K. The combined effects of mixed layering and a trioctahedral structure on interlayer K exchange were ascertained with coarsely ground mica-vermiculites.

When samples of 10-20 μm ground muscovite were heated at different temperatures, the initial and maximum amounts of K release underwent relatively little change. Coupled with the fact that the initial release of K was quite small, these results show the coarsely ground muscovite particles were not prone to layer weathering and were not recrystallized (to the extent of making much K unexchangeable) by high temperatures (900°C). The rates of K release, however, changed substantially as the heating temperature increased and proved to be related in part to the weight loss. Experiments with samples that were heated for different periods at selected temperatures made the release rate - weight loss relationships even more evident.

Samples of 10-20 μm muscovite that were heated at low temperatures (400°C) exhibited a reduction in K release rate--a thermal response not previously reported--while the mineral lost weight by dehydration. Separate experiments with samples that were first heated at low temperatures and then rehydrated, however, showed that the presence of hydration water has no effect on the exchangeability of interlayer K. At temperatures above 400°C , the K release rate increased as the mineral lost weight by dehydroxylation. This increase did not occur when muscovite samples were heated in a water saturated atmosphere to prevent dehydroxylation. Moreover, a close correlation between the weight loss and release rate values was observed when the thermal treatments enhanced the release of K. Thus, it was concluded that the dehydroxylation process is responsible for the thermally induced increase in the rate of K release by muscovite. An increase in temperature beyond that needed for a dehydroxylation of the mica produced a major reduction in the K release rate.

Complete K release curves for heated samples of the 10-20 μm muscovite confirmed earlier observations by Kozak (1976) that heat treatments can retard the release of some interlayer K while they hasten the release of K from other parts of the same sample. This situation was examined in greater detail by calculating the average rate with which successive 20 meq increments of K were released from selected

samples of heated muscovite. These calculations yielded the surprising information that the thermal treatments did not affect an ever widening band around the rim of the particles as would be expected if the mica were altered by a homogeneous mechanism. Instead, the K ions throughout each mica particle experienced a complex sequence of reductions, increases and finally reductions in exchangeability as the intensity of the thermal treatment was increased. This behavior was presumably due to the fact that the samples were heated in an unvented oven or furnace, which allowed the water vapor to build up around the particles. Under these circumstances, there was a low gradient for the loss of structural water by diffusion and the mineral was dehydroxylated by an inhomogeneous mechanism (instead of the rim-core process observed by Kodama and Brydon, 1968, with heated muscovite in a vacuum). A different heating procedure would probably yield somewhat different K release data, but the interpretation of these data in terms of mineral properties should be the same.

Whereas dehydroxylation in the coarse muscovite particles was clearly responsible for the increases in K exchangeability, no connection between the weight losses and the decreases in K release was observed. Noting that the effects of dehydroxylation can be accounted for by an increase in

interlayer spacing (due to the escaping molecules of structural water), it seems likely that the decreases in K release rate are due to a contraction of the mineral. The silica tetrahedra in muscovite crystals are rotated from an ideal hexagonal arrangement. When the mineral is heated, these tetrahedra can untwist, the hexagonal hole in the oxygen plane can enlarge and the interlayer K can sink deeper into the hole and become less exchangeable. When X-ray diffraction measurements were carried out with muscovite samples that were heated at low and very high temperatures, however, no reductions in basal spacings were observed. The diffraction patterns for the high temperature samples provided evidence that structural alterations did occur (by modifications in the relative intensity of the various X-ray reflections); thus, a thickening of the octahedral sheet could have easily masked a decrease in interlayer spacing and left the basal spacing unchanged. Until a structural analysis of the heated muscovite proves otherwise, reductions in the interlayer spacing (by changes in tetrahedra rotation or tilting) are still the best explanation for the decreases in K exchangeability.

Several size-fractions (10-20, 5-10, 2-5, 0.2-2, <2 μm) of ground muscovite were subjected to comparable thermal treatments to determine how the heat induced changes in K exchangeability are affected by the size of mineral particles.

Complete K release curves for the unheated samples depicted the usual effects of particle size on interlayer K release. The initial release of K increased, the maximum degree of K release decreased and the rate of K release increased as the particle size was reduced. The increase in initial release can be attributed to the occurrence of more layer weathering in the smaller particles. The layer weathering, in turn, is deemed to be responsible for the lower maximum level of K release. Much of the K is released by edge weathering and at a rate that is enhanced by shorter diffusion distances and longer weathering fronts in the smaller particles. Obviously, there were many ways the thermal treatments could interact with the effects of particle size.

The various size-fractions of muscovite responded to the thermal treatments in a similar manner, in that the K release rate first decreased, then increased and finally decreased when all the samples were heated at progressively higher temperatures. As the particle size decreased, however, the initial decrease became more pronounced, the increase occurred at lower temperatures and the final decrease occurred at higher temperatures. From the weight loss determinations it was evident that the increase in release rate occurred at lower temperatures in the smaller particles because these temperatures were adequate for dehydroxylation. Otherwise, the effects of particle size on the thermal

response of muscovite did not correlate with the weight losses. For instance, the smaller particles contained much more hydration water, but this difference had no impact on the K release data. Thus, the comparison of several size-fractions made it clear that thermal studies of K exchangeability must consider the role of particle size but did not explain all the particle size effects. For further information, the $<2\text{ }\mu\text{m}$ muscovite fraction was studied in more detail and compared with the 10-20 μm sample.

When the $<2\text{ }\mu\text{m}$ samples were heated at temperatures that dehydroxylated the minerals, increases in the rate of K release occurred as they did in coarse particles. In addition, however, these same temperatures increased the release of K by edge weathering in the small particles--a change that was not possible in the coarse particles because they released nearly all their K irrespective of the heat treatment. When other heating temperatures were used, the two size-fractions differed in their response because they were not equally susceptible to layer weathering. Due to a difference in particle size, unheated samples of $<2\text{ }\mu\text{m}$ muscovite released 24% of their K by layer weathering, whereas the 10-20 μm samples released only 2%. When the samples were heated at progressively higher temperatures (to 900°C), the layer weathering decreased in just the small particles. Taken together, these thermally induced decreases in K exchangeability account for

much of the effects of a decrease in particle size on the heat induced changes in interlayer K exchangeability. In other words, it has been established that thermal treatments provide a means of assessing the relevance of layer weathering and incomplete edge weathering in ground mica samples.

The heating experiments with $<2\text{ }\mu\text{m}$ ground muscovite provided useful information about the exchangeability of K in small particles. Unheated samples of the $<2\text{ }\mu\text{m}$ mica released a maximum of 76% of its K. This incomplete release of K has been attributed to the presence of layer weathering (an increase in layer weathering causing a decrease in maximum release). When the small particles were heated, however, a simultaneous reduction in both the layer weathering and the maximum release occurred. These results must be construed as evidence that the limited release of K by small particles is not determined by layer weathering. On the other hand, a graphical analysis of the effects of heating on edge weathering shows the small particles would release all their K if the effects of dehydroxylation could be achieved without the inhibiting effects of temperature up to 400°C . This calculation and the observation that a decrease in the maximum release occurs as the edge release is reduced by temperatures over 500°C would suggest instead that the release of K in small mica particles is limited by the interlayer spacing. This suggestion is compatible with

the likelihood that the mica structures would shift toward a hexagonal arrangement as the constraints of large particles are reduced by a decrease in particle size or thermal treatments.

In a comparison of the response of several size-fractions of muscovite to different temperatures, it was observed that higher temperatures had to be used to reduce the release rate of dehydroxylated samples when the particles were smaller. These results prompt the unlikely conclusion that smaller particles are more resistant to high temperature alterations even though they are more susceptible to changes by low temperatures (e.g., dehydroxylation at lower temperatures). These observations, however, must be viewed with caution because the release rates were measured with an arbitrary 24-hour extraction period and were affected by changes in the amounts of layer weathering. Similar determinations of the release rate with a 3-hour extraction period and a correction for layer weathering indicated that it was more likely that there was no effect of particle size on the high temperature alterations. Since it has been suggested that the decrease in release rate at high heating temperatures is due to structural adjustments that reduce the interlayer spacing, no effects of particle size should really be expected.

Samples of naturally occurring $<2\text{ }\mu\text{m}$ particles of Tumut

illite were heated and compared with heated $<2\text{ }\mu\text{m}$ samples of ground muscovite in regard to their K exchangeability. Since the Tumut illite is a well-crystallized mica and has essentially no mixed layering, the results of this comparison were construed as a measure of the effects of mica grinding on the exchangeability of interlayer K.

Both the Tumut and the muscovite samples exhibited an increase in K exchangeability when they were heated enough to dehydroxylate the minerals. This effect of thermal treatments appears to be a characteristic of dioctahedral minerals and not a function of edge alterations from grinding. Otherwise, the two minerals yielded quite different thermal responses because the particles differed in their susceptibility to layer weathering.

The unheated Tumut illite released very little K initially (2% versus 24% by the muscovite) and exhibited an increase in the initial release when heated instead of the decrease observed with muscovite. Moreover, the amount of K extracted by the initial extraction period increased when the Tumut particles were dehydroxylated by thermal treatments--a response that is indicative of edge weathering. Taken together, these results show there was little layer weathering in the Tumut particles. By comparison, the ground muscovite particles of the same size released large amounts of K by layer weathering and the degree of layer weathering

varied with the amount of grinding that was used to prepare the various size-fractions of ground muscovite. In other words, grinding can alter the exchangeability of interlayer K by changing the degree to which the K is released by layer weathering. Through this layer weathering, the grinding treatments produced other differences in the K release by heated Tumut and muscovite samples. In particular, thermal treatments reduced the release of K by layer weathering and, thereby, limited the maximum release of K in just the ground samples. In the absence of grinding, the Tumut samples exhibited no reduction in K release at the lower temperatures and released essentially all their K (97% versus 84% for ground $<2\ \mu\text{m}$ muscovite) when they were dehydroxylated.

The relative responses of $<2\ \mu\text{m}$ Tumut and muscovite samples provide a basis for a simple procedure for the detection of layer weathering. If the initial release of K by micaceous minerals in NaCl-NaTPB solutions is reduced by preheating the mineral for 24 hours at temperatures up to 400°C , the mineral released K by layer weathering. Otherwise, the initial release of K occurred by edge weathering and the amount of K release is increased by the same heat treatment. This procedure should be very useful with fine-grained illites, soil clays, etc., because they release their K too rapidly to permit the use of other means of characterizing the mechanism by which they initiate their release of K.

Since many fine-grained micaceous minerals have some degree of mixed layering in their crystal structure, the effects of this mixed layering on interlayer K exchangeability was investigated with thermally treated minerals. For this study, samples of $<2\ \mu\text{m}$ Grundite illite were heated and compared with $<2\ \mu\text{m}$ samples of Tumut and muscovite. Like the Tumut illite, Grundite is a naturally-occurring, fine-grained micaceous mineral but it has 25 to 30% expanded layers.

The effects of various thermal treatments on the exchangeability of interlayer K in Grundite illite proved to be very similar to those of Tumut. Indeed, the thermal responses provided no evidence that mixed layering in the Grundite had any effect on the release of K. As with Tumut, heat treatments enhanced the initial release of K by Grundite--showing there was little or no layer weathering in this naturally fine-grained mineral either. This information represents a major contribution of the thermal study because questions about the presence of layer weathering and its role in the incomplete release of K in Grundite have been debated for some time. Since there was no layer weathering in either illite, the limited release of 86 and 68% of the K in unheated Tumut and Grundite, respectively, can no longer be attributed to a separation of some layers by layer weathering. If so, the presence of mixed layering

should not be held responsible for the smaller total release of K in Grundite either. Instead, these results support the earlier conclusions from the $<2\text{ }\mu\text{m}$ muscovite data that another size-dependent parameter of the mineral particles must be involved. Since dehydroxylation increases the interlayer spacing of heated micas and enhances the maximum degree of K release by Tumut and Grundite samples to 97 and 96%, respectively, it is probably the interlayer spacing of small particles that limits the maximum release of K.

The interlayer spacing of contracted micaceous minerals is determined by the extent to which the interlayer K ions are imbedded in the oxygen planes and, thus, by the degree to which the mineral structure deviates from a hexagonal arrangement. It was stated earlier that thermal treatments can cause the silica tetrahedra in micas to untwist from their ditrigonal arrangement, the K to sink deeper into the oxygen plane and the interlayer space to decrease. A decrease in the particle size of unheated mica could have the same effect because the impact of the octahedral sheet on the configuration of the tetrahedral sheet should decrease as the particle size is reduced. If the decrease in particle size is achieved by grinding, the particles become more prone to layer weathering and an association between layer weathering and incomplete K release can be expected. The limited

release of K by these small ground particles and naturally small particles (where no layer weathering occurs), however, should be attributed to the effects imposed by the inter-layer spacing, not layer weathering.

This study of the role of mineral properties in the exchange of interlayer K focused on the dioctahedral micaceous minerals, but four trioctahedral mica-vermiculites (SCH, SCL, MH and ML) were included because preliminary experiments with the SCH mineral yielded thermal responses that were similar to dioctahedral minerals. These minerals had mixed-layer structures, but their content of expanded layers varied from nearly 75% in the SCL mineral to none in the ML mineral. Thus, they provided a situation where the minerals were similar but varied from the SCL that behaved like dioctahedral micas when heated to the ML that should behave like biotite (a trioctahedral mica). Samples of these minerals were subjected to various thermal treatments and the effects of these treatments on their K exchangeability were compared with the thermal responses of muscovite, illite and biotite. Very coarsely ground ($<1/6''$) samples were used to minimize the effects of grinding and to retard the release of K enough to make the thermal effects visible. Particular attention was given to the relevance of mixed layering and trioctahedral character of the minerals.

When the SCH, SCL and MH minerals were heated for 24

hours at different temperatures, they responded to essentially the same temperatures and exhibited similar changes in their K exchangeability. Their responses differed in terms of degree but gave no indication that their differences in mixed layering were involved. Thus, these mica-vermiculites can be considered as a group and described by the SCL results.

The SCL results confirmed earlier observations (with the SCH mineral) that heated samples of these mica-vermiculites do not behave like trioctahedral micas. Instead, some of their key responses to thermal treatments were more like those of coarse muscovite particles. The maximum release of K was relatively constant (near 100%) in samples that were heated at temperatures up to 800°C and the rate of K release first increased and then decreased as the temperature was raised above 450°C. In other respects, the SCL mineral differed from muscovite in that the maximum release decreased at temperatures over 800°C and the release rate went through a sequence of increases and decreases when the temperature was increased to 400°C. The low temperature (<400°C) changes in K exchangeability are actually similar to those of dioctahedral illite but more extensive. Overall, the thermal responses of the SCL mineral are complex and not readily explained in terms of mineral properties.

The increase in K exchangeability that occurred when

samples of SCL mineral, various size-fractions of muscovite and two illites were heated at temperatures above 400°C is the most distinctive and universal response of heated dioctahedral minerals. Weight loss determinations have shown that this increase in K exchangeability in dioctahedral minerals stems from a dehydroxylation of the mineral. This explanation does not apply to the increase in the SCL mineral. In fact, the weight loss curve for the SCL mineral provides no indication that losses of hydration or structural water play a part in any of the thermally induced changes in K exchangeability. On the other hand, the various increases and decreases in K exchangeability that were observed when the SCL samples were heated at temperatures up to 600°C did not occur in heated samples of the ML mineral where there was no mixed layering. While this information is quite limited, it suggests that mixed layering plays a major role in the exchangeability of K in mica-vermiculites.

The ML mineral differed from the other mica-vermiculites by having a higher K content (197 meq/100 g), more structural Fe^{++} (91 mmoles/100 g) and little mixed layering. According to these properties, this mineral was essentially a biotite. The response of the ML mineral to thermal treatments, however, was not like that of biotite or the other mica-vermiculites. As stated earlier, the ML mineral differed from the other mica-vermiculites by exhibiting no changes in K exchangeability at temperatures up to 600°C.

By not inhibiting increases in K release rate at these temperatures, the ML mineral behaved like biotite but the ML mineral resisted thermal alterations to much higher temperatures than biotite. Temperatures in excess of 350 and 600°C reduced the exchangeability of K in the biotite and ML samples, respectively. This difference cannot be attributed to the amounts of Fe^{++} in the minerals because Fe^{++} oxidation was initiated by temperatures of only 300°C in both minerals. Moreover, most of the Fe^{++} was oxidized before changes in K exchangeability occurred in the ML mineral. While these results do not delineate the mineral properties that govern the exchangeability of K in the ML mineral, they do indicate that the oxidation of structural Fe^{++} in tri-octahedral micaceous minerals is not as universally involved as many believe.

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